

Optimization and scaling-up of porous solid electrolyte electrochemical reactors for hydrogen peroxide electrosynthesis

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The solid electrolyte reactor, initially proposed and developed by Haotian Wang's group for the oxygen reduction reaction to produce pure hydrogen peroxide, has been extended to versatile applications such as CO₂ reduction reactions and CO₂ capture. Building on this prototype, the authors report on the evaluation and improvement of the PSE reactor for practical applications. They investigated material selection, assembly parameters, flow field patterns, and operating conditions of PSE reactors, optimizing the reactor from both engineering and technical perspectives. They believe it has the potential to overcome the limitations of scaling up and transitioning the PSE reactor to practical applications. However, despite some technical research and exploration, the work is overly detailed and lacks the innovation and depth required for publication in Nature Communications. It is recommended to submit it to a more technically specialized journal.

Additional comments:

1. The authors should clarify whether the data in Table 1 are from commercial information or experimental tests. If the data are solely from commercial information, the authors' work on the performance of different types of solid electrolytes is limited to device performance evaluation, lacking scientific significance and insight.
2. The authors mention that higher resistance of solid electrolytes generates more Joule heat, but the testing method is only illustrated in Fig. S3. Several issues need clarification: How is temperature stability ensured during testing? How does temperature change with electrolysis time? Is the temperature field uniform in large-area devices? Without controlling these variables, direct comparison of temperature data is meaningless.
3. In Fig. 1e, the authors fit a negative logarithmic curve using the SA group density and R_s resistance data of four solid electrolytes. This is confusing. What is the significance of this fitting? What is the physical meaning of the fitting equation? SA group density is not the only difference among the four solid electrolytes, nor is it the only factor affecting R_s . Mathematical fitting of these data is not instructive unless the authors can find more types of solid electrolytes that fit this relationship and provide a reasonable physical explanation.
4. In Fig. 2, the authors show the effect of solid electrolyte packing density on performance and control the liquid flow rate. Is this the inlet or outlet flow rate? High flow resistance in the solid electrolyte layer at higher packing densities can cause back pressure, leading to a lower outlet flow rate. If calculated based on the inlet flow rate, the measured performance may be overestimated. Considering the pressure changes caused by packing density, the authors should also explore whether the internal pressure of the solid electrolyte layer affects performance.
5. Page 10, Line 201 mentions the impact of solid electrolyte size and packing density on contact and refers to Fig. S10. However, Fig. S10 describes the temperature of different solid electrolytes during operation, which is unrelated to this sentence.
6. The Nyquist plots in Figs. S9, S11, and S12 should provide data over the entire test range and explain the curve behavior rather than simply listing them.
7. In the study of the effect of anion membrane treatment on its structure using ATR-IR, the authors did not provide specific experimental protocols (e.g., treatment time). To illustrate that HO₂⁻ generated under strong alkaline conditions can damage the membrane structure, the authors could characterize the effect of H₂O₂ solutions at different pH levels on the anion membrane structure.
8. The authors' investigation of the degradation of anion exchange membranes in PSE is limited to a single experimental method. It is recommended to supplement ion conductivity tests. Additionally, the authors did not provide practical solutions,

making this part of the work scientifically insufficient.

9. When studying the effects of various parameters, what was the area of the electrolytic cell used? Do these conclusions still apply when the area is further expanded? Are they still instructive for large-area reactors?

10. The description of the final stack setup is minimal, including electrode preparation and operating conditions. Was overheating an issue during testing? How was the electrolytic cell cooled? Was the product collection uniform in large-area reactors, and how was performance testing error minimized? Notably, none of the data in this paper were tested with error bars.

11. The figure numbers are incorrect; the content of Figs. S1 and S2 mentioned in the text does not match the SI.

Reviewer #2

(Remarks to the Author)

This study optimized a PSE reactors for hydrogen peroxide electrosynthesis. Results showed that PSE spheres with high surface sulfonate group densities and AEMs with hydrophilic polymer backbones improve the conduction of H^+ and HO_2^- ions, enhancing H_2O_2 production. The use of natural air diffusion cathodes and catalyst-coated membrane anodes allows H_2O_2 synthesis without gas pumps or sulfuric acid, simplifying reactor design and operation. By incorporating serpentine channels to improve flow patterns, the reactor was successfully scaled up to produce ~2.5 kg of pure H_2O_2 , suitable for applications like water treatment and disinfection. Energy costs were significantly lower (0.2–0.8 USD/kg), and the H_2O_2 solutions produced were salt-free, making them suitable for various uses. However, AEM degradation due to nucleophilic attack by HO_2^- ions remains a challenge for long-term stability.

Overall, the paper is clear, well-written, and free of major issues. The explanation is more empirically based but remains convincing. The topic is of high interest and importance, not only from an academic perspective but also due to its strong industrial and practical relevance. I really liked this paper, and I recommend its acceptance because of the significant technological advances it brings to the field.

However, I have a few points that need clarification:

Regarding the PSE spheres, is there any degradation of the particles, loss of efficiency, etc.?

Why were only AEMs employed? Wouldn't proton exchange membranes be even more efficient in terms of ion transfer and so why that high alkaline pH?

Typically, H_2O_2 is unstable at alkaline pH, which is why it is sold with the addition of small quantities of organic acids. The acidic functional groups not only enhance conductivity but also help stabilize H_2O_2 by preventing radical formation and membrane degradation. However, wouldn't it be simpler to work directly in acidic conditions, possibly considering other electrocatalysts that remain active in alkaline conditions?

Reviewer #3

(Remarks to the Author)

Comments:

This work investigated the main influencing factors, feasibility and scalability of a porous solid-state electrolyte (PSE) reactor for electrosynthesis of H_2O_2 . The research topics is meaningful and the discussions insightful. However, there are some problems exist in the article, and more comprehensive discussion or explanations should be added. The work needs to be carefully checked. I think it needs a major revision before further consideration. Specific comments are as follows.

1. Line 29, " H_2O_2 decomposition" or "Decomposition of AEMs by H_2O_2 ". Please check and revise to an appropriate statement.
2. Line 30-35. The innovative points of this work need to be further condensed. What is the purpose of the serpentine channels? The abstract and introduction sections need to reflect more scientific thinking.
3. Please double check the graphical abstract and the SI Figures S2-5, which are currently quite different. In addition, please clarify whether H_2O or H^+ is involved in the reaction on the anode side.
4. In the current version, the supplementary figures appear in a different order in the manuscript than that in the SI, which creates a reading impediment. Moreover, some of the supplementary figures are difficult to correspond to the manuscript. For example, Fig. S2 on line 146, Fig. S9 and Fig. S10 on line 201.
5. Please check the abbreviations to ensure that the full name is available on the first occurrence.
6. Please check Fig. S10, there is a mismatch between materials and properties.
7. The unit should be Ω rather than $\Omega\text{ cm}^2$ in all EIS pictures and tables.
8. Fig. 2. Higher packing density and lower diameter result in better performance. Consider continuing to scale up or down the parameters, the current parameters may not be optimal.
9. Line 210-213. The reason for choosing these two parameters?
10. Fig. S11g. The amount of H_2O_2 produced by the 35-75 μm samples increased rapidly after 25 min. Please check or explain why. In addition, check the 'ACE%' in the right side for the vertical coordinate.
11. Line 363-365. Please indicate this condition in the caption of Fig. 3f.
12. Fig.3f. Please range the vertical coordinates near the starting point of the sample.
13. Fig. 3g. Please show the C=N bond in the virgin and used samples.
14. Check Figures 4a and 4b, which show almost same results.
15. Fig. 4. Is there a possibility of cations interfering with the PEM?
16. Line 422. Fig. 6f should be Fig. 6e.

17. Please describe in detail the costing process for large area reactors.
18. Please evaluate the stability of the 1200 cm² PSE reactor.

Reviewer #4

(Remarks to the Author)

The manuscript "Optimization and scaling-up of porous solid electrolyte electrochemical reactors for hydrogen peroxide electrosynthesis" provides a systematic study and optimization of a PSE reactor for the electrosynthesis of H₂O₂. The results show that the PSE with high surface sulfonate group density and the AEM with hydrophilic polymer backbone facilitate the conduction of H⁺ and HO₂⁻ for efficient H₂O₂ electrosynthesis. The use of natural air diffusion cathodes and catalyst-coating membrane anodes allows the PSE reactor to produce H₂O₂ without the need for an air pump to supply oxygen/air or the use of sulphuric acid as a dissolving solution, which greatly simplifies the configuration of the PSE reactor and facilitates its operation. By designing serpentine channels to improve the flow pattern in the PSE layer, the PSE reactor can be successfully scaled up without a significant reduction in the electrosynthesis performance of H₂O₂. This study is in principle interesting for a wide readership, especially provides an economically competitive and attractive method to produce H₂O₂. But some of the conclusions are hard to follow and requiring more discussion toward the results. Hence, before considering published in the Nature Communications, following issues need to be addressed:

- 1) In Fig. 3 and Fig. S17, the mean square displacement and radial distribution functions of the two AEMs (Sustainion X-37T and AMI-7001) were analysed. To demonstrate that the experimental tendency of all AEMs can be explained by the mechanism proposed by the authors, please add the data of classical MD simulations for Piperion A-40, Pention 7215-30, FAA-3-50, FAA-3-PK-130.
- 2) It would be more convincing to find more theoretical support, such as ab initio molecular dynamics, for describing how different quaternary amine groups affect the HO₂⁻ transfer.
- 3) In all MD simulations, the authors used the system including only 10 monomers to represent the AEM. In such a small system, it is not possible to accurately simulate its actual material properties. It is better to clarify the reliability of model and method.
- 4) On page 13, line 251, the authors suggest that the quaternary amine group in EAM affects the strength of hydration of HO₂⁻. The stronger the HO₂⁻ hydration, the greater the electrostatic effect. Please give the relevant theoretical justification on the conclusion.
- 5) The manuscript does not explain some of the mechanisms clearly and contains some spelling errors, which affects the overall quality and readability, such as:
 - a) In Fig. 3g, the 1036 cm⁻¹ band is proposed to be labelled.
 - b) On page 21, line 422, the manuscript refers to figure 6f, but it is absent.
 - c) In Fig. S2b, the cathode was only energised with oxygen and no proton source was observed to provide the reaction to produce HO₂⁻. The authors should give a clear schematic diagram of local reaction-transport process.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

In the revised manuscript, the authors have expanded the electrode area to 100 cm² and designed a 12-unit modular PSE stack with a total electrode area of 1200 cm² for H₂O₂ electrosynthesis, maintaining a stable faradaic efficiency over 500 hours, which is astounding! However, the manuscript does not provide detailed information about the stack's design or operational parameters, and some data presented is dubious. In my opinion, if the authors have indeed succeeded in constructing this stack and achieving stable operation, it would represent a major breakthrough. That being said, this is precisely why I remain cautious. I believe the authors should provide a video demonstrating the construction and operation of the stack or third-party validation of their results. If the authors can offer this evidence, I would be more than happy to recommend the paper for publication.

Detailed comments:

1. The authors need to present the flow field design for the large-area reactor. Using a serpentine flow channel raises questions about the uniformity of current distribution and adequate mass transfer across such a large area. According to the supplementary information (SI, Section S6), the oxygen flow rate for the 1200 cm² reactor is specified as 300 mL min⁻¹. Even under ideal conditions of 100% single-pass conversion and 100% FE, this corresponds to an oxygen supply of only 0.0122 mol min⁻¹ (2362.9 C min⁻¹), which supports a current of merely 39.3 A. This translates to a current density of less than 33 mA cm⁻², which seems insufficient for the reported performance.
2. The use of infrared thermal imaging to observe heat effects is of limited value, as it captures the temperature of the reactor's external surface after heat dissipation through the metal casing, which does not reflect the actual conditions at the reaction interface. For instance, in Fig. S28, the maximum observed temperature for the 1200 cm² reactor is only 28.5°C, which is lower than the maximum temperature recorded in the 4 cm² reactor (Fig. S9d). This discrepancy appears inconsistent. Furthermore, Fig. S28c shows that, with cooling water, the reactor's overall temperature is just 15°C. The authors should clarify whether such low temperatures affect catalytic performance and consider maintaining a controlled reaction temperature near room temperature to ensure comparability.
3. The specific methods used to construct the 1200 cm² reactor stack should be disclosed, as many technical details remain

unclear. For example, are the individual cells connected in series or parallel? The manuscript states (Page 25, Line 475) that at a current density of 200 mA cm⁻², the cell voltage is 5.5 V. If the cells are connected in series, why is the cell voltage so low? Conversely, if the cells are in parallel, such a high voltage is unexpected. The authors should provide video footage of the stack in operation and present the voltage-time curve for the 480-hour stability test.

4. The flow rate of deionized water in the middle layer of the stack during operation and the pressure distribution in the middle layer are not discussed. These critical experimental details should be provided to ensure reproducibility. While Fig. S29 provides energy consumption data for reactors of different areas, the authors should include the detailed calculation methods used to derive this data.

(Remarks on code availability)

Reviewer #2

(Remarks to the Author)

Authors have addressed the most part of my question, so in my view it can be accepted

Reviewer #3

(Remarks to the Author)

All concerns have been addressed and the manuscript can be accepted.

(Remarks on code availability)

Reviewer #4

(Remarks to the Author)

The authors have submitted a revised version of manuscript NCOMMS-24-51548A. The authors responded carefully to all queries and provided additional calculations to support their arguments. The authors have answered all the questions I raised in my initial review of this paper, and I consider the manuscript suitable for publication in Nature Communications.

(Remarks on code availability)

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

In response to my comment, the authors have provided videos demonstrating both the assembly and operation of the PSE stack. Given this additional evidence, I now find the manuscript to be robust and well-supported. I am pleased to recommend the paper for publication.

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December 15, 2024

Manuscript submitted to Nature Communications: **NCOMMS-24-51548A**, entitled “**Optimization and scaling-up of porous solid electrolyte electrochemical reactors for hydrogen peroxide electrosynthesis**”.

Dear Editor,

We appreciate the valuable time that **Reviewer 1** has taken to review this paper. We have accommodated these review comments as follows:

General comments: The solid electrolyte reactor, initially proposed and developed by Haotian Wang’s group for the oxygen reduction reaction to produce pure hydrogen peroxide, has been extended to versatile applications such as CO₂ reduction reactions and CO₂ capture. Building on this prototype, the authors report on the evaluation and improvement of the PSE reactor for practical applications. They investigated material selection, assembly parameters, flow field patterns, and operating conditions of PSE reactors, optimizing the reactor from both engineering and technical perspectives. They believe it has the potential to overcome the limitations of scaling up and transitioning the PSE reactor to practical applications. However, despite some technical research and exploration, the work is overly detailed and lacks the innovation and depth required for publication in Nature Communications. It is recommended to submit it to a more technically specialized journal.

Response: We appreciate the thoughtful summary and insightful comments of Reviewer 1. As described in the manuscript, while the PSE reactor developed by Dr. Haotian Wang’s group has shown great promise for H₂O₂ electrosynthesis, there are still significant challenges that need to be overcome for transferring this technology to practical applications. To this end, this study addressed some of the critical issues of the PSE reactor (e.g., stability, scalability, and safety) that are of paramount importance for practical applications. Specifically, we evaluated the long-



term stability of PSE reactors and revealed the decay mechanism of AEMs during H_2O_2 electrosynthesis, optimized the reactor design to efficiently produce H_2O_2 without the use of air pump and sulfuric acid, and successfully scaled up the PSE reactor without a significant reduction in the electrosynthesis performance of H_2O_2 . We believe that these findings are novel and critical for developing the PSE reactors for practical applications, and are of interests for a wide readership from both an academic and industrial perspective.

In response to the reviewer's comments, we have revised the introduction of the manuscript to highlight the novelty and importance of this work. Page 5–6 line 95–124 has been revised to read: “While the PSE reactor has shown great promise for H_2O_2 electrosynthesis, it still needs systematic evaluations and improvement to be applied in the field.^{7,10,11} For practical applications, the stability, scalability, and safety of electrochemical reactors are of paramount importance. However, to date, no studies have evaluated the long-term stability of the PSE reactor. Although some studies have shown that the PSE reactor can be stably operated for 100–200 h under 30 mA/cm^2 ,^{9,12} the long-term stability of PSE reactors under industrially relevant conditions remains unclear as it may take longer time and/or higher current densities for the decay of reactor components (e.g., GDE and membranes) to become appreciable.^{8,13} Moreover, the previous study showed that the performance of H_2O_2 electrosynthesis declined seriously as the PSE reactor was scaled up: as the electrode area of the PSE reactor was enlarged from 4 to 80 cm^2 , the cell voltage and energy consumption of H_2O_2 electrosynthesis increased significantly from ~ 2.1 to 5.7 V and from 3.9 to $10.1 \text{ kWh/kg H}_2\text{O}_2$ at the same applied current density of 200 mA/cm^2 .⁹ Yet, the causes for the declined performance have not been well understood. Furthermore, sulfuric acid solutions are currently used as the anolyte in the PSE reactor,^{9,14} which is undesired in some scenarios (e.g., household applications) due to the safety concern. Overall, the above information highlights that there are still some issues and challenges that need to be resolved and overcome for scaling up and transferring the PSE reactor to practical applications.

The main objectives of this study were (i) to investigate the long-term stability and possible decay mechanism of PSE reactor during H_2O_2 electrosynthesis under industrially relevant



conditions, (ii) to reveal the causes for the declined performance of enlarged PSE reactors, and (iii) to optimize the reactor design to overcome some barriers that impede the scaling up and transfer of the technology to practical applications. To this end, the effects of material selection, assembly parameters, flow field patterns, and operating conditions of PSE reactors on H_2O_2 electrosynthesis were systematically evaluated. The ion conduction, reaction thermodynamics, and flow field distribution in the PSE reactor were investigated using molecular dynamics (MD), density functional theory (DFT), and computational fluid dynamics (CFD) tools. Based on the obtained findings, the reactor design was optimized and a modular PSE reactor with a total electrode area of 1200 cm^2 was developed. The feasibility of the scaled-up PSE reactor for potential niche applications were then evaluated under likely operating conditions.”

Specific comments

C1: The authors should clarify whether the data in Table 1 are from commercial information or experimental tests. If the data are solely from commercial information, the authors’ work on the performance of different types of solid electrolytes is limited to device performance evaluation, lacking scientific significance and insight.

R1: Thank you for the suggestion. We have indicated that the data in Table 1 are from experimental tests in the revised manuscript. For example, page 30 line 578–581 now reads: “The Brunauer-Emmett-Teller surface areas of the PSE microspheres were measured with a Nova Station A analyzer (Quantachrome Co., Ltd., USA). The ion exchange capacity of the PSEs was measured using a titration method described previously (see SI for more detail).^{51,52}”

In addition, we have added footnotes to Table 1, which now reads:

Table 1. Parameters of PSE microspheres tested in this study.

PSE	Ion exchange capacity (meq/g)	Surface area (m^2/g)	SA group density (meq/m^2) ^a	R_s (Ω) ^b
Dowex 50W×8	3.1	0.025	124	1.77
Amberlite IR 120H	4.1	0.066	62.1	2.66
Sennate D001×7	4.4	0.118	37.3	3.28
Purolite CT-175	4.7	23.4	0.2	8.25
Amberlyst 39WET	5.5	0.112	49.1	3.92
Amberlyst 15WET	4.5	55	0.08	7.84
Amberlyst 36WET	5.5	20.1	0.27	6.84
Lewatit K2621	5.5	31	0.18	7.51



Dowex 50W×4	1.4	0.021	66.67	1.76
Purolite CT-275	5.1	24.7	0.21	2.65

^acalculated based on the measured ion exchange capacity and surface area of PSE microspheres.

^bmeasured with a packing density of PSE microspheres of 1100 mg/mL, see SI Fig. S7 and S8 for more detail.

C2: The authors mention that higher resistance of solid electrolytes generates more Joule heat, but the testing method is only illustrated in Fig. S3. Several issues need clarification: How is temperature stability ensured during testing? How does temperature change with electrolysis time? Is the temperature field uniform in large-area devices? Without controlling these variables, direct comparison of temperature data is meaningless.

R2: We appreciate the thoughtfulness of Reviewer 1. As per the reviewer's questions, we have added more information about temperature of the reactor during H₂O₂ electrosynthesis in the revised manuscript and SI. Page 29 line 553–555 has been revised to read: “In some experiments, a thermocouple or pressure meter was inserted into the PSE chamber to measure the temperature and internal pressure of the flow cell (see SI Fig. S2 and Fig. S3)”.

SI page 8–9 line 116–125 and page 30 line 469–475 now reads: “During H₂O₂ electrosynthesis, the temperature inside the PSE reactor increased quickly to a stable level within a few minutes (Fig. S9a). Moreover, the steady temperatures increased with increasing applied current densities due to the more significant Joule heating effect at higher currents (Fig. S9b). Furthermore, the R_s of PSEs has a significant effect on the reactor temperature. Under an applied current density of 200 mA/cm², the stabilized temperatures were ~26–28 °C during H₂O₂ electrosynthesis with Dowex 50W×8, Amberlite IR 120H, and Sennate D001×7, but reached ~45 °C with Purolite CT-175 (Fig. S9c) because of its considerably higher R_s than the other PSEs (see Table 1). Additionally, a homogenous temperature field of the PSE reactor can be observed with various PSEs, evidenced by the infrared thermal imaging (Fig. S9d).

As shown by the infrared thermal image (Fig. S9d), the temperature field inside the small PSE reactor (4 cm²) was generally uniform during H₂O₂ electrosynthesis. However, the temperature field became uneven when the PSE reactor was scaled up to 1200 cm² (Fig. S28b), which may result in damages to some components of the reactor (e.g., the AEM) due to local overheating. Therefore, a cooling system was designed for the scaled-up reactor (see Fig. S27a and Fig. S28a for the reactor schematic). By recirculating cooling water (~4 °C) through the



PSE reactor, a uniform temperature field was obtained during H_2O_2 electrosynthesis (Fig. S28c).”

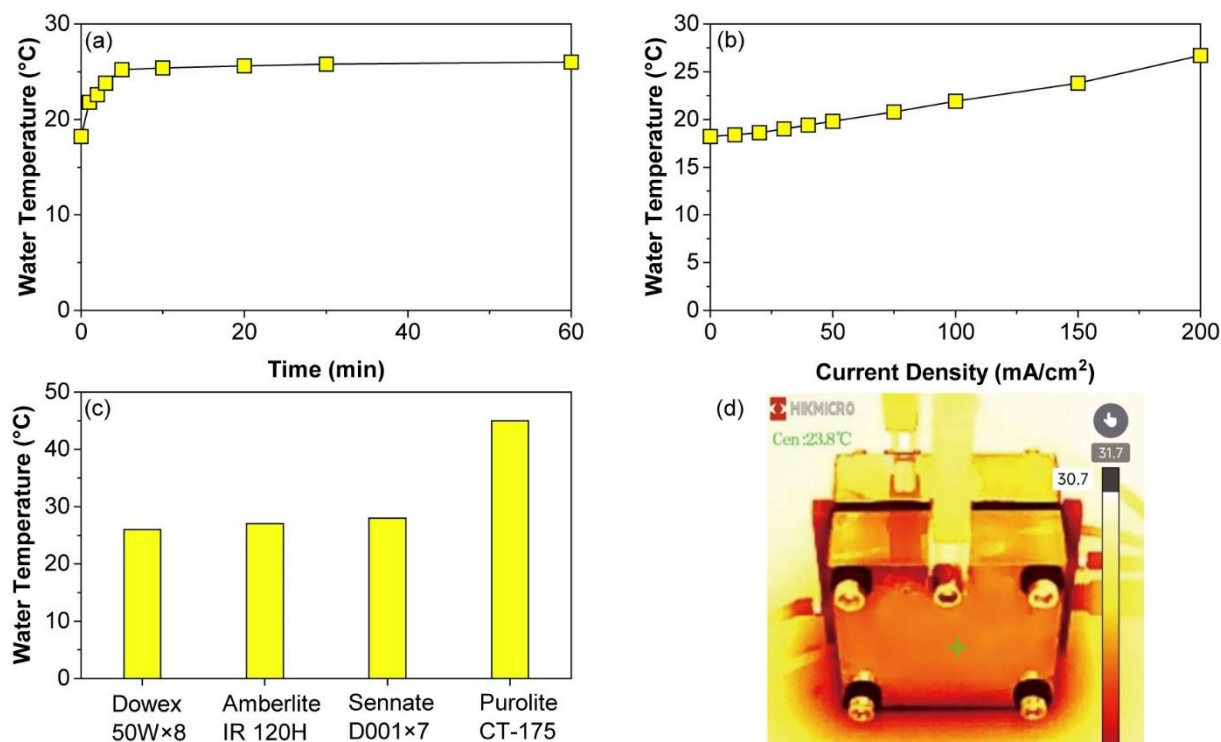


Fig. S9. Reactor temperatures as a function of (a) operation time, (b) current density, and (c) PSE type during H_2O_2 electrosynthesis, (d) infrared thermal imaging of the PSE cell. Operating conditions: PSE = Dowex 50W×8 for Figs. S9a, b, and d; current density = 200 mA/cm² for Figs. S9a, c, and d.

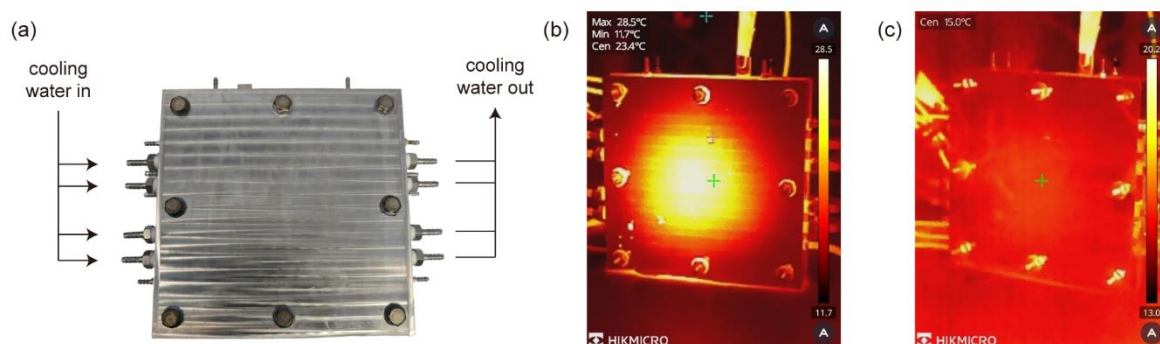


Fig. S28. (a) The inlet and outlet of cooling water of the electrode stack, infrared thermal imaging of the PSE cell (b) without and (c) with cooling water recirculation.



C3: In Fig. 1e, the authors fit a negative logarithmic curve using the SA group density and R_s resistance data of four solid electrolytes. This is confusing. What is the significance of this fitting? What is the physical meaning of the fitting equation? SA group density is not the only difference among the four solid electrolytes, nor is it the only factor affecting R_s . Mathematical fitting of these data is not instructive unless the authors can find more types of solid electrolytes that fit this relationship and provide a reasonable physical explanation.

R3: We appreciate the constructive suggestion of Reviewer 1. As suggested, we measured the SA group density and R_s of six more PSEs, and fitted the data together with the data of the four previously tested PSEs. The result show that they still follow a negative logarithmic relationship ($R^2 = 0.9235$, see below). Notably, similar logarithmic relationships have been reported between the concentration of ion conducting composition and conductivity of various solid ion conductors (e.g., conducting polymer electrolytes and conducting glasses) and suggested to be related to the ion transfer mechanism of the conductors.^{1,2}

In response to the reviewer's comments, we have revised the manuscript with newly obtained data. Page 8 line 164–177 now reads: “Because H^+ conduction on the PSE surface proceeds mainly through a hopping diffusion process between neighboring SA groups (i.e., the Grotthuss mechanism),¹⁷⁻¹⁹ the decrease of surface density of SA groups may hamper H^+ conduction (see Fig. 1d for the schematic illustration). To verify this inference, we measured the resistance of H^+ conduction (R_s) of ten different types of PSE microspheres that have varied surface densities of SA groups (0.08–124 meq/m², Table 1) by an electrochemical impedance spectroscopy (EIS) method (see SI Fig. S7 for the experimental schematic). In the Nyquist plot (SI Fig. S8), the R_s of PSE was determined from the intersection of the fitting curves and Z' axis.^{20,21} As expected, R_s of the PSEs increases with decreasing their surface density of SA groups (Table 1). Moreover, a negative logarithmic relationship is found between the R_s and SA group density of the various PSEs (Fig. 1e). Similar logarithmic relationships have also been reported between the conductivity and the concentration of ion conducting composition of various solid ion conductors (e.g., crystalline polymer electrolytes and conducting glasses) and suggested to be related to the ion transfer mechanism of the conductors.^{22,23}”

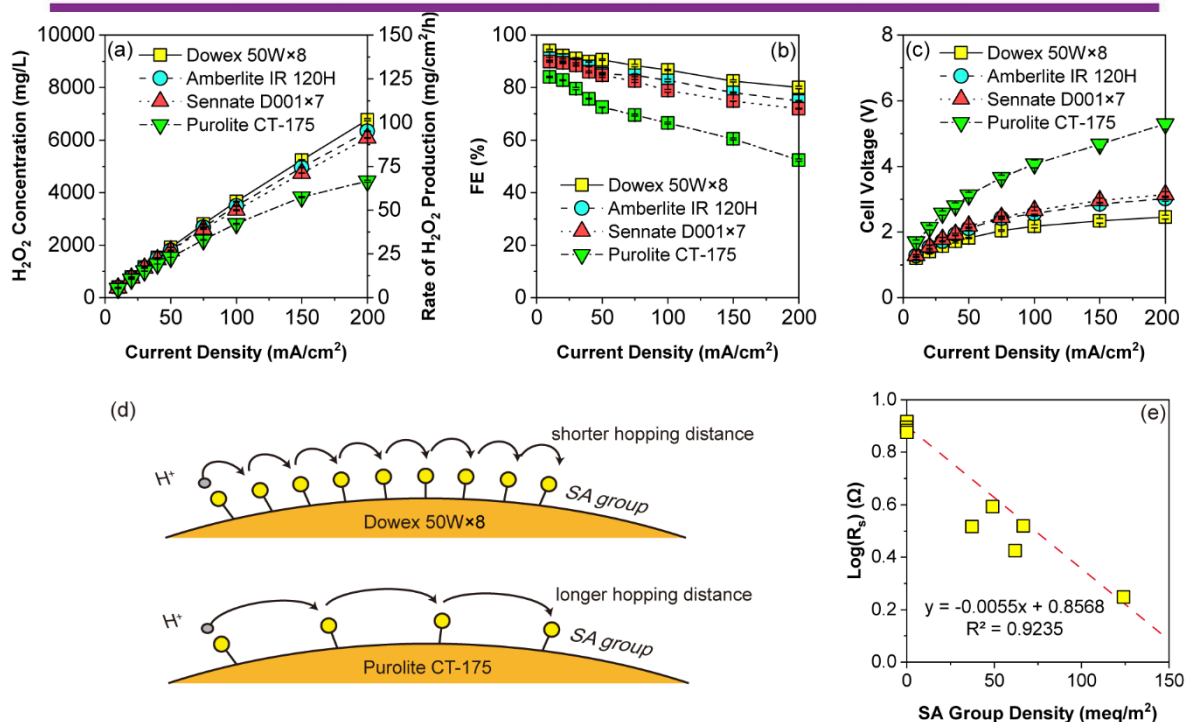


Fig. 1. The effects of applied current densities on (a) H_2O_2 concentrations and production rates, (b) FEs, and (c) cell voltages during H_2O_2 electrosynthesis with various PSEs, (d) illustrations of H^+ transfer on Dowex 50W×8 and Purolite CT-175, and (e) the negative logarithmic relationship between the surface SA density and R_s of H^+ conduction of ten types of PSEs. For H_2O_2 electrosynthesis in a 4 cm² reactor, the PSEs (~300–1000 μm) were packed with a packing density of ~1100 mg/mL, and the water flow rate was fixed to 1 mL/min. The cathode and anode were fed with pure oxygen (50 mL/min) and 0.5 M H_2SO_4 (recirculated), respectively, and no AEM was used.

C4: In Fig. 2, the authors show the effect of solid electrolyte packing density on performance and control the liquid flow rate. Is this the inlet or outlet flow rate? High flow resistance in the solid electrolyte layer at higher packing densities can cause back pressure, leading to a lower outlet flow rate. If calculated based on the inlet flow rate, the measured performance may be overestimated. Considering the pressure changes caused by packing density, the authors should also explore whether the internal pressure of the solid electrolyte layer affects performance.

R4: We appreciate the thoughtfulness of Reviewer 1. During H_2O_2 electrosynthesis, DI water was continuously passed through the PSE chamber. Therefore, the flow rate at the inlet and outlet was the same, and all calculations were based on experimentally measured flow rates.



In response to the reviewer's comments, we have revised the manuscript to explain these issues. Page 29 line 559–563 now reads: “During H_2O_2 electrosynthesis, an oxygen gas (50 mL/min) and 0.5 M H_2SO_4 solution were fed through the cathode and anode compartment, respectively, while DI water was passed through the PSE chamber (see SI Figure S1c). The backpressure of the GDE compartment was monitored using a gas pressure meter (see SI Figure S3). The flow rate of DI water was adjusted to preset values by varying the pressure of the peristaltic pump.”

Page 11–12 line 214–222 has been revised to read: “However, the decrease of particle size and increase of packing density of PSE microspheres decreases the porosity of the PSE layer. Hence, higher pressures were needed to drive the DI water to pass through the PSE reactor (see SI Fig. S10e). When PSE microspheres with diameters larger than 150 μm were packed in the reactor, the water flow was very stable during H_2O_2 electrosynthesis (see SI Fig. S10e). However, when PSE microspheres with smaller diameters were packed, some microspheres could be washed away from the PSE chamber by the DI water flow, and then gradually clogged the outlet of the reactor. As a result, the water flow decreased gradually during H_2O_2 electrosynthesis with PSE microspheres less than 150 μm (SI Fig. S10e).”

SI page 10 line 145–153 now reads: “With decreasing the PSE microsphere diameter, higher pressures were required to drive the water to pass through the PSE reactor. Nevertheless, the increase of pressures did not considerably influence the performance of H_2O_2 electrosynthesis. For example, Figs. S10e and f show that FEs and H_2O_2 concentrations were generally the same under the different pressures. However, when the smallest PSE microspheres (35–75 μm) were used, the outlet of the reactor would be gradually clogged by microspheres washed away from the PSE chamber. Consequently, the flow rate decreased considerably during H_2O_2 electrosynthesis with the smallest PSE microspheres (Fig. S10e), which in turn increased H_2O_2 concentrations in the reactor effluent considerably, while FEs remained almost unchanged (Fig. S10f).”

C5: Page 10, Line 201 mentions the impact of solid electrolyte size and packing density on contact and refers to Fig. S10. However, Fig. S10 describes the temperature of different solid electrolytes during operation, which is unrelated to this sentence.

R5: Thank you for the kind reminder. The effects of PSE size and packing density on contact were actually shown in Fig. S11 in the former edition. We have rearranged the figures of



Supporting Information and corrected the typo in the revised manuscript. Page 11 line 210–212 now reads: “The more efficient H_2O_2 electrosynthesis with smaller and/or more densely packed PSE microspheres can be mainly attributed to the increase of contact points among the packed microspheres (see SI Fig. S10a).”

C6: The Nyquist plots in Figs. S9, S11, and S12 should provide data over the entire test range and explain the curve behavior rather than simply listing them.

R6: Thank you for the suggestion. The Nyquist plots have been redrawn to shown the entire test range. For example, Fig. S9 has been redrawn as below, and page 9 line 167–171 has been revised to read: “To verify this inference, we measured the resistance of H^+ conduction (R_s) of ten different types of PSE microspheres that have varied surface densities of SA groups ($0.08\text{--}124\text{ meq/m}^2$, Table 1) by an electrochemical impedance spectroscopy (EIS) method (see SI Fig. S7 for the experimental schematic). In the Nyquist plot (SI Fig. S8), the R_s of PSE was determined from the intersection of the fitting curves and Z' axis.^{20,21}”

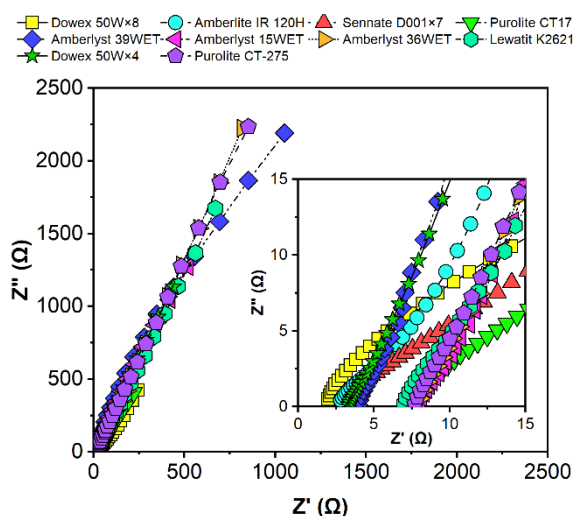


Fig. S8. Nyquist plots of various PSEs.

C7: In the study of the effect of anion membrane treatment on its structure using ATR-IR, the authors did not provide specific experimental protocols (e.g., treatment time). To illustrate that HO_2^- generated under strong alkaline conditions can damage the membrane structure, the authors could characterize the effect of H_2O_2 solutions at different pH levels on the anion membrane structure.

R7: We appreciate the suggestion of Reviewer 1. As suggested, we soaked the AEMs



(Sustainion XC-37T) in H_2O_2 solutions at varying pHs (7–13) for 120 h, and then analyzed their structure and ion conductivity with ATR-IR and EIS techniques, respectively. The results are now included in the revised manuscript. Page 17 line 312–316 now reads: “To reveal the mechanism of AEM degradation, the structure of the virgin and used Sustainion XC-37T AEM, as well as AEMs that had been soaked in NaOH (pH = 13) and H_2O_2 solutions (1%) with varying pH levels (pH = 7–13) for 120 h, or treated by ultraviolet/ H_2O_2 (1%, pH = 7) process (120 h) was examined using attenuated total reflection infrared spectroscopy (ATR-IR) (Fig. 3f).”

Page 17 – 18 line 326–340 has been revised to read: “Interestingly, while the IR spectra of AEMs soaked in NaOH (pH = 13) and H_2O_2 solutions with pHs lower than the pK_a of H_2O_2 (11.6) exhibit no significant changes as compared to that of the virgin AEM, the IR spectra of AEM soaked in H_2O_2 solutions at pH 13 exhibits similar changes as have been observed for the used AEM, e.g., the increase of 1036 cm^{-1} band and the emergence of 1260, 1345, and 2960 cm^{-1} bands. These comparisons indicate that OH^- and H_2O_2 are not very reactive with AEMs, whereas HO_2^- (which is the predominant species of $\text{H}_2\text{O}_2/\text{HO}_2^-$ at pH higher than the pK_a of H_2O_2) is probably the main species that causes AEM degradation during H_2O_2 electrosynthesis. Consistently, DFT calculations show that due to the strong nucleophilicity of HO_2^- , it can attack the QA groups of AEMs and thus cause AEM degradation (see SI Fig. S21–S23 and Table S3–S4 for more detail). Corresponding to its significant structural changes, the ion conductivity of the AEM soaked in H_2O_2 solutions at pH 13 decreased substantially, as has been shown for the used AEM (Fig. 3g). In comparison, the ion conductivity of AEMs soaked in other solutions exhibit insignificant or only small decreases (H_2O_2 solution at pH 11) as compared to that of the virgin AEM. These observations corroborate that HO_2^- is the main species responsible for AEM degradation during H_2O_2 electrosynthesis.”

C8: The authors’ investigation of the degradation of anion exchange membranes in PSE is limited to a single experimental method. It is recommended to supplement ion conductivity tests. Additionally, the authors did not provide practical solutions, making this part of the work scientifically insufficient.

R8: As suggested by the reviewer, the ion conductivity of AEMs has been measured and reported in the revised manuscript (see R7). In this study, we have found that the stability of AEMs is the bottleneck of PSE reactors for long-term stable operations, and revealed that HO_2^-



attack is the main degradation mechanism of AEMs during H_2O_2 electrosynthesis. These findings are important for the development of more durable AEMs to improve the stability of PSE reactors.

Nevertheless, the design and development of HO_2^- -resistant AEMs is not our expertise and beyond the scope of this study. Therefore, we only briefly discussed several possible options that may be helpful to improve the stability of PSE reactors during H_2O_2 electrosynthesis and suggested future research needs in the manuscript. For example, page 18–19 line 350–358 reads: “With decreasing the concentrations of produced H_2O_2 solutions (~ 100 mg/L) by using smaller current densities (15 mA/cm^2) during H_2O_2 electrosynthesis, the lifetime of Sustainion XC-37T AEM could be extended to ~ 1500 h (Fig. 3h). However, this duration is still insufficient for many industrial applications. Therefore, more stable AEMs need to be developed for H_2O_2 electrosynthesis with the PSE reactor. In addition, Rawah et al. proposed to replace the AEM with a PTFE layer to improve the stability of the PSE reactor for H_2O_2 electrosynthesis.¹¹ However, the PSE reactor with the PTFE layer was tested for only 50 h at a current density of 70 mA/cm^2 . Further studies are still required to verify the long-term stability of the PSE reactor with the PTFE layer.”

C9: When studying the effects of various parameters, what was the area of the electrolytic cell used? Do these conclusions still apply when the area is further expanded? Are they still instructive for large-area reactors?

R9: Thank you for the question. The effects of various parameters were evaluated using the small PSE reactor with 4 cm^2 electrodes since it is much easier and more economical to assemble/disassemble the reactor to test various PSEs, AEMs, and other parameters. Based on the optimized parameters determined with the small reactor, the PSE reactor was enlarged firstly to 25 cm^2 , and further to 1200 cm^2 . As shown in Fig. 6, by designing a serpentine flow channel to optimize the flow field in the enlarged reactors, the PSE reactor can be successfully scaled up without a significant reduction in the performance of H_2O_2 electrosynthesis. These observations indicate that the optimized parameters and conclusions obtained with the small reactor still apply for the enlarged reactors.

In response to the reviewer’s comments, we have indicated the reactor size in the caption of relevant figures in the revised manuscript. In addition, page 22 line 437–439 has been revised to read: “To test the scalability of the PSE reactor, we first designed an enlarged PSE reactor



with 25 cm² electrodes based on the optimized parameters determined for the small PSE reactor (4 cm²).” Page 25 line 465–470 has been revised to read: “As shown in Fig. 6d, the serpentine flow channel considerably improves the uniformity of flow field. As a result, the rates and FEs of H₂O₂ production increased substantially, while the cell voltages decreased considerably (Fig. 6a-c). These observations indicate that the PSE reactor can be successfully scaled up based on the optimized parameters determined with the small reactor (4 cm²) and highlight the importance of optimizing the flow field when scaling up the PSE reactor.”

C10: The description of the final stack setup is minimal, including electrode preparation and operating conditions. Was overheating an issue during testing? How was the electrolytic cell cooled? Was the product collection uniform in large-area reactors, and how was performance testing error minimized? Notably, none of the data in this paper were tested with error bars.

R10: We appreciate the thoughtfulness of Reviewer 1. In response to the reviewer’s comments, we have added more details on the final stack setup in the revised manuscript. Page 25 line 471–473 has been revised to read: “Based on this finding, we further extended the electrode area to 100 cm² and designed a 12-unit modular electrode stack with a total electrode area of 1200 cm² for H₂O₂ electrosynthesis (see SI Fig. S27 for the stack setup).” SI page 29–30 line 456–465 now reads: “Based on the optimized reactor configurations determined with the small PSE reactor (4 cm²), a modular electrode stack with a total electrode area of 1200 cm² was manufactured (see Fig. S27a). The electrode stack consisted of 12 parallel modular units, and each unit has an effective electrode area of 100 cm². PSE microspheres (Dowex 50W×8, 150–300 μm) were packed with a packing density of ~1100 mg/mL in the serpentine channels between the AEM and PEM. During H₂O₂ electrosynthesis, an oxygen gas (300 mL/min) and water (25 mL/min) were fed to the cathode and anode of the units, respectively, and DI water was passed through the serpentine channels to collect produced H₂O₂. To prevent overheating of the electrode stack by the Joule heating effect, cooling water (~4 °C) was recirculated through the reactor using a peristaltic pump.”

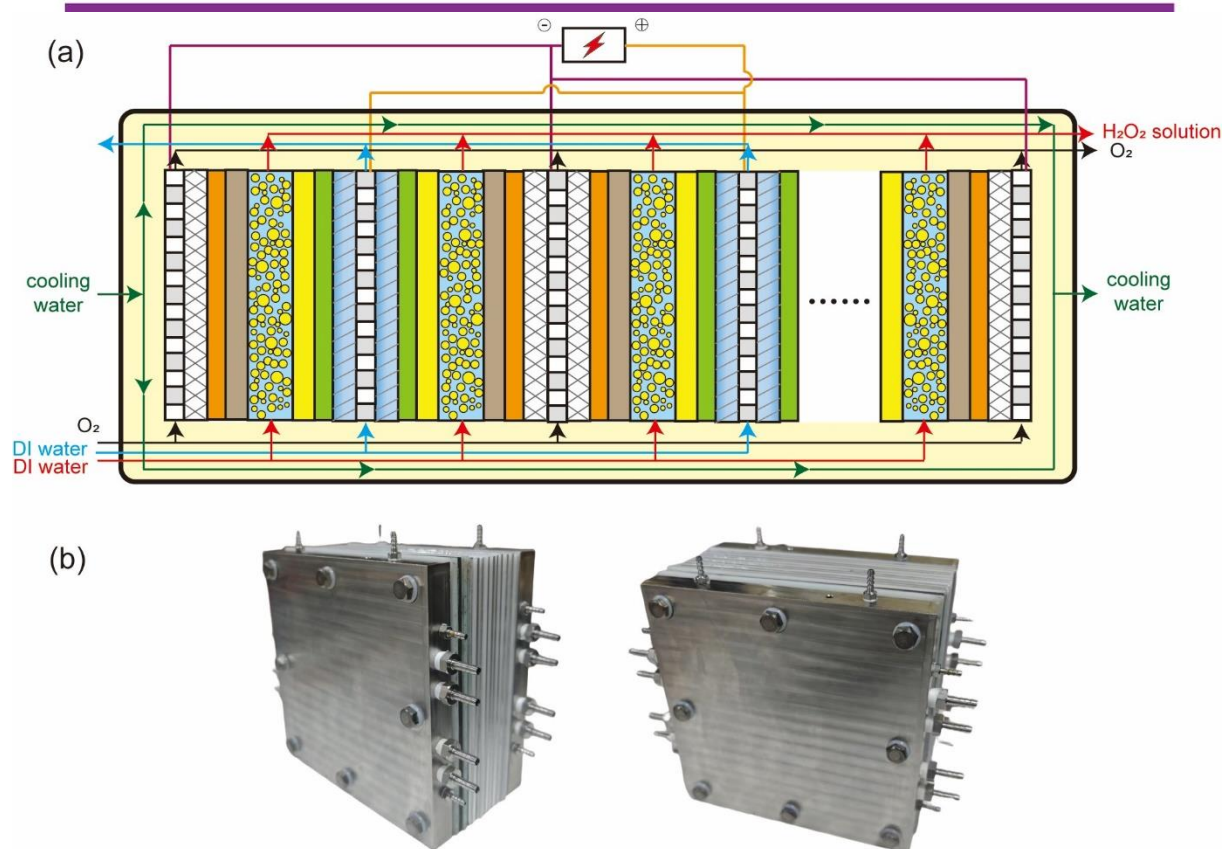


Fig. S27. The (a) schematic and (b) photos of the 12-unit modular electrode stack.

Regarding the experimental reproducibility, most experiments were repeated at least twice, with the exception of the long-term stability experiments that lasted for hundreds of hours. The experimental errors are usually very small and the error bars are mostly overlapped by the data symbols in the figures. Therefore, the error bars are not shown in the original figures. In response to the reviewer's comments, we have redrawn the figures to show the error bars when they are available. Please see the revised manuscript and SI.

C11: The figure numbers are incorrect; the content of Figs. S1 and S2 mentioned in the text does not match the SI.

R11: Thank you for the kind reminder. We have checked all the figure numbers and corrected the mismatched text in the revised manuscript.

We trust that these revisions accommodate the recommendations of Reviewer 1.



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Sincerely,

Yujue Wang, Ph.D.

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Reference

- 1 Swenson, J. & Börjesson, L. Correlation between free volume and ionic conductivity in fast ion conducting glasses. *Phys. Rev. Lett.* **77**, 3569-3572 (1996).
- 2 Christie, A. M., Lilley, S. J., Staunton, E., Andreev, Y. G. & Bruce, P. G. Increasing the conductivity of crystalline polymer electrolytes. *Nature* **433**, 50-53 (2005).

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December 15, 2024

Manuscript submitted to Nature Communications: **NCOMMS-24-51548A**, entitled “**Optimization and scaling-up of porous solid electrolyte electrochemical reactors for hydrogen peroxide electrosynthesis**”.

Dear Editor,

We appreciate the valuable time that **Reviewer 2** has taken to review this paper. We have accommodated these review comments as follows:

General comments: This study optimized a PSE reactors for hydrogen peroxide electrosynthesis. Results showed that PSE spheres with high surface sulfonate group densities and AEMs with hydrophilic polymer backbones improve the conduction of H^+ and HO_2^- ions, enhancing H_2O_2 production. The use of natural air diffusion cathodes and catalyst-coated membrane anodes allows H_2O_2 synthesis without gas pumps or sulfuric acid, simplifying reactor design and operation. By incorporating serpentine channels to improve flow patterns, the reactor was successfully scaled up to produce ~ 2.5 kg of pure H_2O_2 , suitable for applications like water treatment and disinfection. Energy costs were significantly lower (0.2–0.8 USD/kg), and the H_2O_2 solutions produced were salt-free, making them suitable for various uses. However, AEM degradation due to nucleophilic attack by HO_2^- ions remains a challenge for long-term stability.

Overall, the paper is clear, well-written, and free of major issues. The explanation is more empirically based but remains convincing. The topic is of high interest and importance, not only from an academic perspective but also due to its strong industrial and practical relevance. I really liked this paper, and I recommend its acceptance because of the significant technological advances it brings to the field.

However, I have a few points that need clarification.



Response: We appreciate the valuable time that the reviewer took in reviewing this manuscript and the positive feedback and overall assessment. We have revised the manuscript to accommodate the reviewer's comments as detailed below.

Specific comments

C1: Regarding the PSE spheres, is there any degradation of the particles, loss of efficiency, etc.?

R1: We appreciate the thoughtfulness of Reviewer 2. The PSE spheres exhibited high stability during H_2O_2 electrosynthesis. There are insignificant changes in the appearance and ion conductivity of PSE microspheres after long-term experiments. In response to the reviewer's comments, we have added some characterization results of the PSE microspheres before and after 500 h of H_2O_2 electrosynthesis in the revised manuscript and SI. Page 16 line 290–292 now reads: “EIS and linear sweep voltammetry (LSV) analysis indicated that there are no significant changes in the ion conductivity of the PSE microspheres and in the ORR activity of the GDE cathode before and after the long-term experiments (SI Fig. S19).” In addition, SI page 19 line 293–295 now reads: “Fig. S19 shows that the PSE microspheres exhibited insignificant changes in the appearance and ion conductivity after 500 h of H_2O_2 electrosynthesis. In addition, the GDE also maintained similar ORR activity after the experiments.”

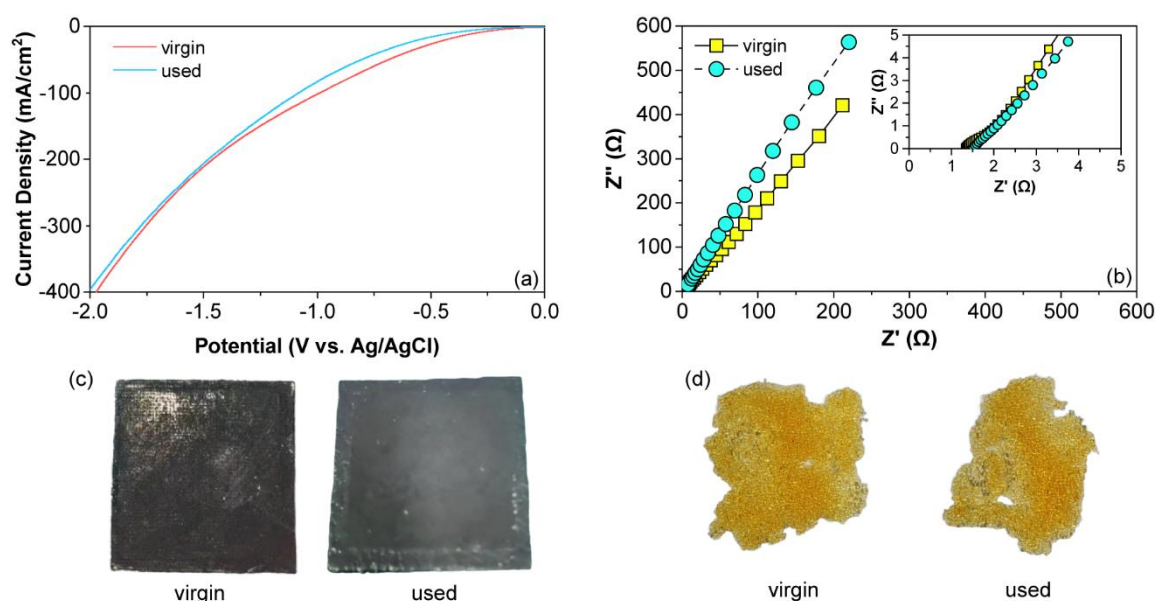


Fig. S19. (a) LSV curves of GDE cathode, (b) EIS plot of PSE (Dowex 50W×8), photos of (c) GDE cathode and (d) PSE (Dowex 50W×8) before and after 500 h of H_2O_2 electrosynthesis



experiments.

C2: Why were only AEMs employed? Wouldn't proton exchange membranes be even more efficient in terms of ion transfer and so why that high alkaline pH?

R2: Thank you for the question. In this study, we employed a catalyst-coated membrane (CCM) anode configuration, where the catalyst (IrO_2) was directly hot pressed on a PEM (Nafion N115) to serve as the anode of the PSE reactor. Therefore, the PEM was not indicated individually in the assembling schematic previously shown in Fig. S2. In response to the reviewer's comments, we have redrawn Fig. S2 to make it clear that a PEM was used to prepare the CCM anode in the PSE reactor. SI Page 3 line 52–64 now reads: “The assembling method of PSE reactor is shown in SI Fig. S1a. Catalyst-coated membrane (CCM) anodes were prepared by directly hot pressing a mixture of IrO_2 catalysts and Nafion ionomer onto a PEM (Nafion N115). GDE cathodes were prepared using a modified catalyst-coated substrate (CCS) strategy by coating XC-72R carbon black power on a carbon paper (HCP135, Hesen Co., Ltd, China). The anode and cathode plates were titanium plates curved with a serpentine flow channel. The anode current collector was a porous titanium felt. PSE microspheres were packed in the PSE chamber and sandwiched by the CCM anode and AEM. These components were assembled with gaskets to form the PSE reactor for H_2O_2 electrosynthesis (Figs. S1a and b).

During H_2O_2 electrosynthesis, water and oxygen were fed to the anode and cathode, respectively (Fig. S1c). H^+ and HO_2^- formed at the anode and cathode then transport and recombine to yield H_2O_2 in the middle PSE layer. Meanwhile, a deionized (DI) water stream was passed through the PSE layer to dissolve the pure H_2O_2 to produce H_2O_2 solutions.”

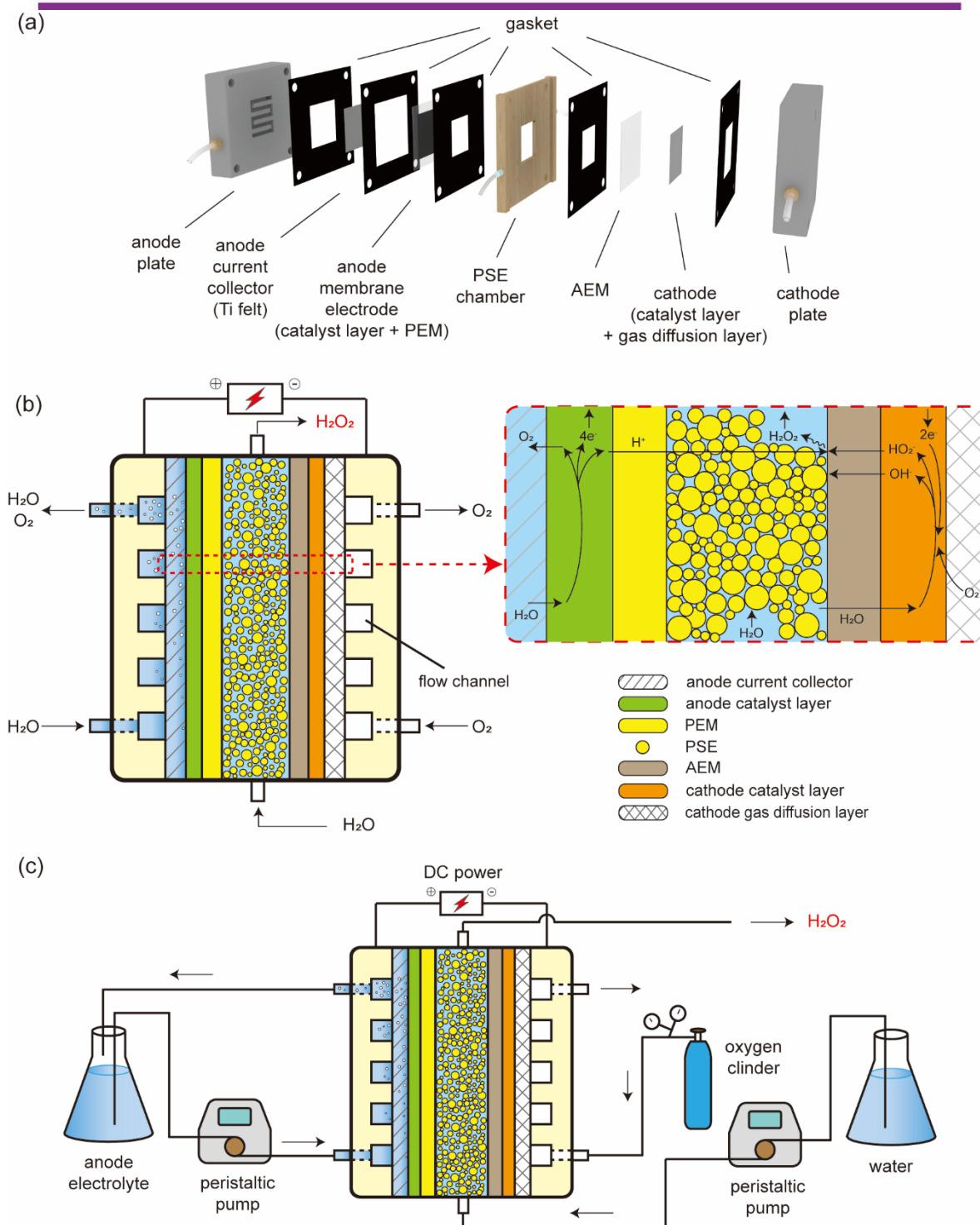


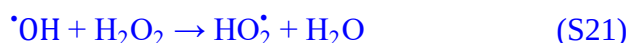
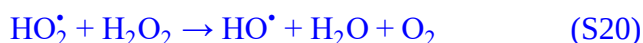
Fig. S1. (a) The components and assembling strategy, (b) H₂O₂ production principle, and (c) operating schematic of the PSE reactor.



C3: Typically, H₂O₂ is unstable at alkaline pH, which is why it is sold with the addition of small quantities of organic acids. The acidic functional groups not only enhance conductivity but also help stabilize H₂O₂ by preventing radical formation and membrane degradation. However, wouldn't it be simpler to work directly in acidic conditions, possibly considering other electrocatalysts that remain active in alkaline conditions?

R3: We appreciate the thought-provoking comments of Reviewer 2. Nevertheless, after careful consideration, we think that it is probably infeasible to run the PSE reactor under acidic conditions in its current configuration. As discussed in the manuscript, due to the high water pressure inside the PSE reactor, an AEM is needed to separate the GDE cathode and water flow in the PSE layer to prevent electrode flooding (see SI Fig. S13), while transporting HO₂[−] (pK_a(H₂O₂) = 11.6) that is produced under alkaline conditions at the GDE cathode to the PSE layer. Although it is possible to replace the carbon catalysts to other catalysts that remain active under acidic conditions, H₂O₂ produced under acidic conditions at the cathode cannot diffuse through the AEM to the PSE layer. If we changed the AEM to some other membranes that allow the diffusion of H₂O₂, H₂O would also penetrate the membranes and thus cause electrode flooding. Therefore, it is possibly infeasible to run the PSE reactor under acidic conditions. Nevertheless, adding small quantities of organic acids to electrosynthesized H₂O₂ solutions is helpful to improve the stability of the products for distribution and sale. We appreciate the suggestion of Reviewer 2.

In response to the reviewer's comments, SI page 31–32 line 488–496 has been revised to read: “Fig. S30a shows the inactivation of *E. coli* with the electrosynthesized H₂O₂ solutions. With H₂O₂ concentrations of 5000–10000 mg/L, *E. coli* can be abated by >7 log within 10–15 min, which confirms that the electrosynthesized H₂O₂ solutions can be directly used for disinfection. According to the standard of peroxide disinfectants of China,³¹ the decomposition of H₂O₂ in qualified disinfectant products at 54 °C should not exceed 15% within 14 d (see Table S6). Fig. S30b shows that H₂O₂ solutions produced with the PSE reactor satisfy this requirement and decomposed less than 10% at 54 °C within 14 days. Nevertheless, H₂O₂ decomposition then accelerated because some decomposition products (e.g., HO₂[•] and [•]OH) can react with H₂O₂ and thus promote its further decomposition.”³²





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In case the electrosynthesized H_2O_2 solutions need to be stored for long time before use, small quantities of organic acids can be added in the H_2O_2 solutions to trap $\cdot\text{OH}$ and $\text{HO}_2\cdot$ and thus prevent these detrimental cascade reactions.^{32,33}

We trust that these revisions accommodate the recommendations of Reviewer 2.

Sincerely,

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December 15, 2024

Manuscript submitted to Nature Communications: **NCOMMS-24-51548A**, entitled “**Optimization and scaling-up of porous solid electrolyte electrochemical reactors for hydrogen peroxide electrosynthesis**”.

Dear Editor,

We appreciate the valuable time that **Reviewer 1** has taken to review this paper. We have accommodated these review comments as follows:

General comments: This work investigated the main influencing factors, feasibility and scalability of a porous solid-state electrolyte (PSE) reactor for electrosynthesis of H_2O_2 . The research topics is meaningful and the discussions insightful. However, there are some problems exist in the article, and more comprehensive discussion or explanations should be added. The work needs to be carefully checked. I think it needs a major revision before further consideration. Specific comments are as follows.

Response: We appreciate the thoughtful summary and insightful comments of Reviewer 3. We have revised the manuscript to accommodate the comments of Reviewer 3, as detailed below.

Specific comments

C1: Line 29, “ H_2O_2 decomposition” or “Decomposition of AEMs by H_2O_2 ”. Please check and revise to an appropriate statement.

R1: Page 2 line 28–30 has been revised to “**Quickly removing produced H_2O_2 from the PSE reactor is critical to mitigating the thermal decomposition of H_2O_2 and thus maintaining high Faradaic efficiencies when scaling up the PSE reactor.**”

C2: Line 30-35. The innovative points of this work need to be further condensed. What is the



purpose of the serpentine channels? The abstract and introduction sections need to reflect more scientific thinking.

R2: We appreciate the constructive suggestion of Reviewer 3. The abstract and introduction sections have been revised as suggested. Page 2 line 30–32 now reads: “By designing serpentine channels to improve the flow pattern in the PSE layer, a PSE reactor with a 12-unit modular electrode stack (total electrode area of 1200 cm²) was successfully developed.”

In addition, page 5–6 line 95–124 in the introduction section has been revised to read: “While the PSE reactor has shown great promise for H₂O₂ electrosynthesis, it still needs systematic evaluations and improvement to be applied in the field.^{7,10,11} For practical applications, the stability, scalability, and safety of electrochemical reactors are of paramount importance. However, to date, no studies have evaluated the long-term stability of the PSE reactor. Although some studies have shown that the PSE reactor can be stably operated for 100–200 h under 30 mA/cm²,^{9,12} the long-term stability of PSE reactors under industrially relevant conditions remains unclear as it may take longer time and/or higher current densities for the decay of reactor components (e.g., GDE and membranes) to become appreciable.^{8,13} Moreover, the previous study showed that the performance of H₂O₂ electrosynthesis declined seriously as the PSE reactor was scaled up: as the electrode area of the PSE reactor was enlarged from 4 to 80 cm², the cell voltage and energy consumption of H₂O₂ electrosynthesis increased significantly from ~2.1 to 5.7 V and from 3.9 to 10.1 kWh/kg H₂O₂ at the same applied current density of 200 mA/cm².⁹ Yet, the causes for the declined performance have not been well understood. Furthermore, sulfuric acid solutions are currently used as the anolyte in the PSE reactor,^{9,14} which is undesired in some scenarios (e.g., household applications) due to the safety concern. Overall, the above information highlights that there are still some issues and challenges that need to be resolved and overcome for scaling up and transferring the PSE reactor to practical applications.

The main objectives of this study were (i) to investigate the long-term stability and possible decay mechanism of PSE reactor during H₂O₂ electrosynthesis under industrially relevant conditions, (ii) to reveal the causes for the declined performance of enlarged PSE reactors, and



(iii) to optimize the reactor design to overcome some barriers that impede the scaling up and transfer of the technology to practical applications. To this end, the effects of material selection, assembly parameters, flow field patterns, and operating conditions of PSE reactors on H_2O_2 electrosynthesis were systematically evaluated. The ion conduction, reaction thermodynamics, and flow field distribution in the PSE reactor were investigated using molecular dynamics (MD), density functional theory (DFT), and computational fluid dynamics (CFD) tools. Based on the obtained findings, the reactor design was optimized and a modular PSE reactor with a total electrode area of 1200 cm^2 was developed. The feasibility of the scaled-up PSE reactor for potential niche applications were then evaluated under likely operating conditions.”

C3: Please double check the graphical abstract and the SI Figures S2-5, which are currently quite different. In addition, please clarify whether H_2O or H^+ is involved in the reaction on the anode side.

R3: Thank you for the kind reminder. We have redrawn some figures to make them in conformity with each other. In addition, Fig. S1b has been redrawn to show the main reactions and transfer processes involved in H_2O_2 electrosynthesis in the PSE reactor, including the involvement of H_2O in the anode reaction.

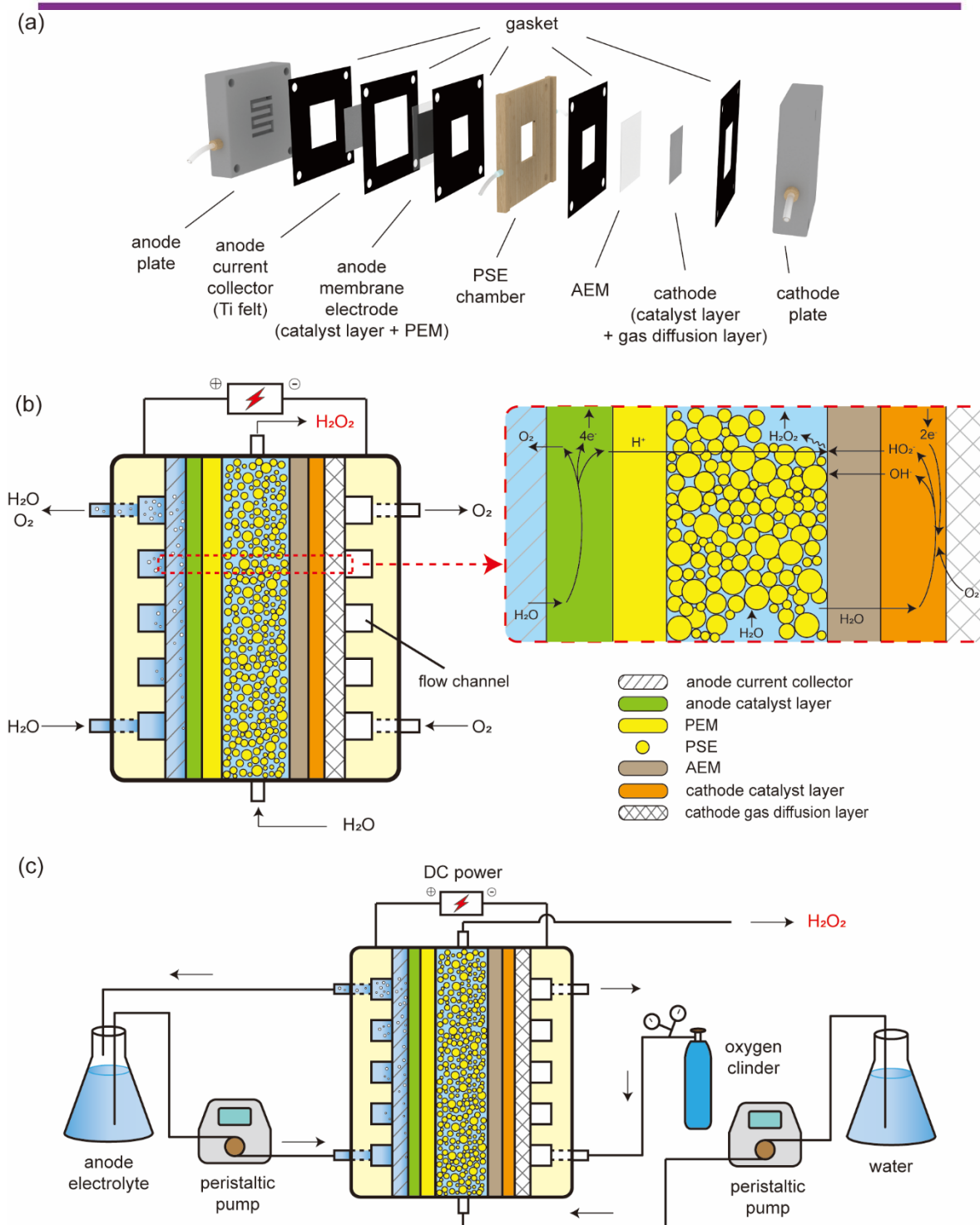


Fig. S1. (a) The components and assembling strategy, (b) H_2O_2 production principle, and (c) operating schematic of the PSE reactor.

C4: In the current version, the supplementary figures appear in a different order in the manuscript than that in the SI, which creates a reading impediment. Moreover, some of the



supplementary figures are difficult to correspond to the manuscript. For example, Fig. S2 on line 146, Fig. S9 and Fig. S10 on line 201.

R4: Thank you for the kinder reminder. We have rearranged the supplemental figures in the order of their appearance in the manuscript.

C5: Please check the abbreviations to ensure that the full name is available on the first occurrence.

R5: Thank you for the suggestion. We have checked all abbreviations to ensure that the full name is given on the first occurrence. Please see the revised manuscript.

C6: Please check Fig. S10, there is a mismatch between materials and properties.

R6: Thank you for the reminder. We have corrected the mismatch in the figure, which is now shown as Fig. S9 in the revised manuscript.

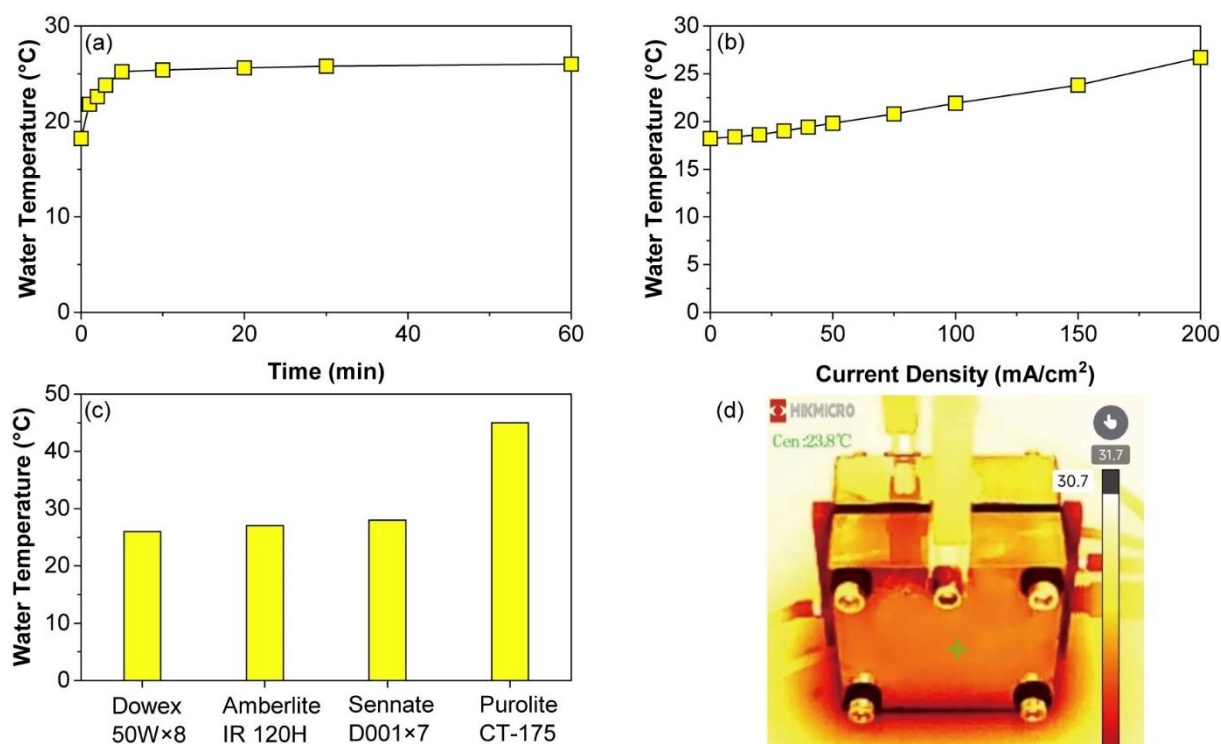


Fig. S9. Reactor temperatures as a function of (a) operation time, (b) current density, and (c) PSE type during H₂O₂ electrosynthesis, (d) infrared thermal imaging of the PSE cell. Operating conditions: PSE = Dowex 50W×8 for Fig.s S9a, b, and d; current density = 200 mA/cm² for Figs. S9a, c, and d.



C7: The unit should be Ω rather than $\Omega \text{ cm}^2$ in all EIS pictures and tables.

R7: The unit has been corrected in the relevant pictures and tables as suggested. Please see the revised manuscript.

C8: Fig. 2. Higher packing density and lower diameter result in better performance. Consider continuing to scale up or down the parameters, the current parameters may not be optimal.

R8: Thanks for the comments. In response to the reviewer's comments, we have discussed the effects of packing densities and particle sizes of PSE microspheres in more detail, and explained the reason for choosing the two parameters used for subsequent experiments. Page 11–12 line 210–229 has been revised to read: “The more efficient H_2O_2 electrosynthesis with smaller and/or more densely packed PSE microspheres can be mainly attributed to the increase of contact points among the packed microspheres (see SI Fig. S10a). Due to the increase of interparticles' contact points, H^+ can more easily transport along the interconnected surfaces of PSE microspheres, thus decreasing the R_s of H^+ conduction and cell voltages (see SI Fig. S10b and c). However, the decrease of particle size and increase of packing density of PSE microspheres decreases the porosity of the PSE layer. Hence, higher pressures were needed to drive the DI water to pass through the PSE reactor (see SI Fig. S10e). When PSE microspheres with diameters larger than $150 \mu\text{m}$ were packed in the reactor, the water flow was very stable during H_2O_2 electrosynthesis (see SI Fig. S10e). However, when PSE microspheres with smaller diameters were packed, some microspheres could be washed away from the PSE chamber by the DI water flow, and then gradually clogged the outlet of the reactor. As a result, the water flow decreased gradually during H_2O_2 electrosynthesis with PSE microspheres less than $150 \mu\text{m}$ (SI Fig. S10e). These observations highlight that the particle size and packing density of PSE microspheres need to be carefully optimized to balance H^+ conduction and water flow during H_2O_2 electrosynthesis. For stable long-term operation, Dowex 50W $\times$ 8 microspheres with particle sizes of $150\text{--}300 \mu\text{m}$ were packed with a packing density of $\sim 1100 \text{ mg/mL}$ for subsequent experiments of H_2O_2 electrosynthesis unless otherwise specified. Note that for PSE microspheres with diameters larger than $150 \mu\text{m}$, $\sim 1100 \text{ mg/mL}$ was the highest packing density of PSE that could be filled in the PSE chamber ($2 \text{ cm} \times 2 \text{ cm} \times 2 \text{ mm}$).”

C9: Line 210–213. The reason for choosing these two parameters?

R9: Please see the response to C8.

C10: Fig. S11g. The amount of H_2O_2 produced by the 35–75 μm samples increased rapidly after 25 min. Please check or explain why. In addition, check the “ACE%” in the right side for the vertical coordinate.

R10: We appreciate the thoughtfulness of Reviewer 3. SI page 10 line 145–153 has been revised to read: “With decreasing the PSE microsphere diameter, higher pressures were required to drive the water to pass through the PSE reactor. Nevertheless, the increase of pressures did not considerably influence the performance of H_2O_2 electrosynthesis. For example, Figs. S10e and f show that FEs and H_2O_2 concentrations were generally the same under the different pressures. However, when the smallest PSE microspheres (35–75 μm) were used, the outlet of the reactor would be gradually clogged by microspheres washed away from the PSE chamber. Consequently, the flow rate deceased considerably during H_2O_2 electrosynthesis with the smallest PSE microspheres (Fig. S10e), which in turn increased H_2O_2 concentrations in the reactor effluent considerably, while FEs remained almost unchanged (Fig. S10f).” In addition, we corrected all the mismatch in the figures.

C11: Line 363–365. Please indicate this condition in the caption of Fig. 3f.

R11: Thank you for the suggestion. We have indicated this condition in the caption of Fig. 3.

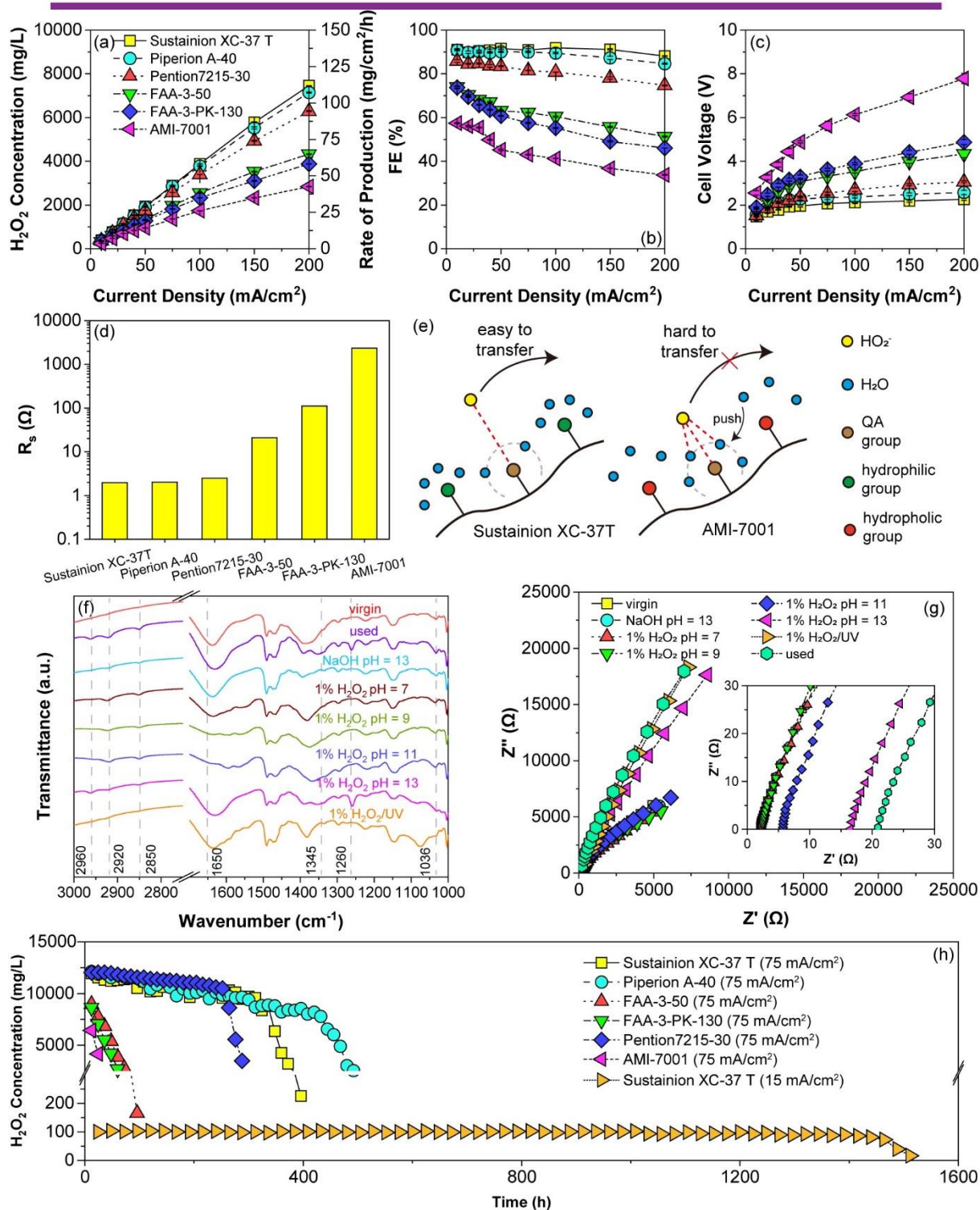


Fig. 3. (a) H_2O_2 concentrations and production rates, (b) FEs, (c) cell voltages as a function of applied current density during H_2O_2 electrosynthesis with the PSE reactor (4 cm^2) with varying AEMs, (d) resistance of HO_2^- conduction of AEMs, (e) illustration of HO_2^- transfer in Sustainion XC-37T and AMI-7001, (f) ATR-IR spectra and (g) Nyquist plots of the virgin



Sustainion XC-37T AEM and those used for H₂O₂ electrosynthesis or treated by different processes, (h) stability of PSE reactors during H₂O₂ electrosynthesis with various AEMs at 15–75 mA/cm². The operating conditions were the same as described in Fig. 2, with the exception that during the stability experiment at 15 mA/cm², a reverse osmosis filtrate of tap water was used to replace DI water as the feeding water to the PSE reactor.

C12: Fig.3f. Please range the vertical coordinates near the starting point of the sample.

R12: Fig. 3h has been redrawn as suggested (see above).

C13: Fig. 3g. Please show the C=N bond in the virgin and used samples.

R13: We appreciate the thoughtfulness of Reviewer 3. Nevertheless, because the stretching band of C=N (~1620–1650 cm⁻¹) overlaps the strong vibration band of –OH, the changes of C=N band cannot be discerned in the spectra. In response to the reviewer’s comments, we have indicated this issue in the manuscript. Page 17 line 316–321 now reads: “Compared with the virgin AEM, the intensity of 1036 and 1260 cm⁻¹ band (stretching vibration of C–N, see SI Table S2 for more information) of the used AEM increased. This change can be probably attributed to the transformation of C=N in the imidazole group to C–N.^{26,27} Note that the C=N stretching band (~1630–1650 cm⁻¹ ²⁸) overlaps the strong vibration band of –OH (bending vibration at ~1630–1640 cm⁻¹ ^{29,30}) and thus cannot be distinguished in the spectra.”

C14: Check Figures 4a and 4b, which show almost same results.

R14: Thank you for the comment. The original Figs. 4a and b show H₂O₂ concentrations, production rates, and FEs. As the production rate and FEs are both calculated based on the H₂O₂ concentrations detected during the process (Eqs. 4 and 5), the curves of the three parameters are the same. In response to the reviewer’s comments, we have redrawn Fig. 4 as below.

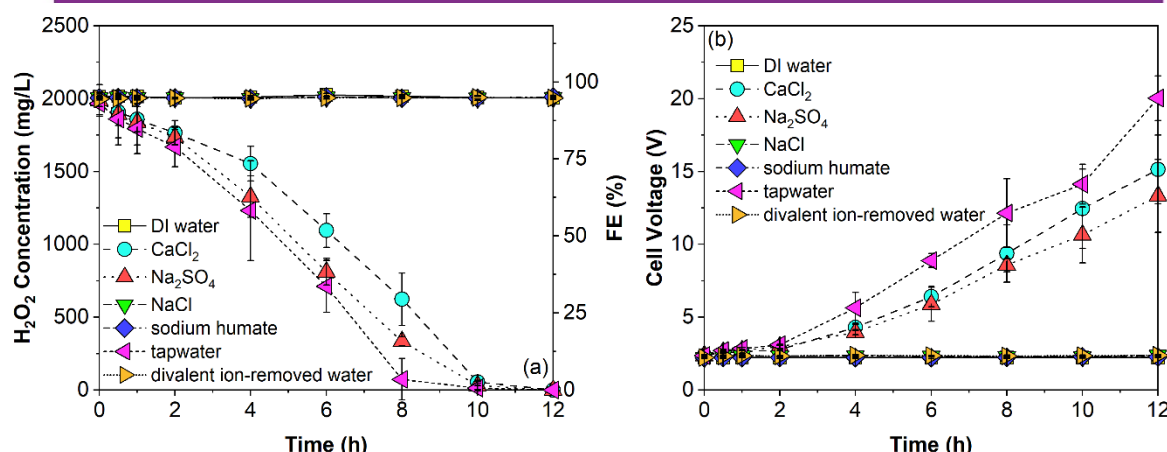


Fig. 4. Effects of water matrices on (a) H_2O_2 concentrations and FEs, (b) cell voltages during H_2O_2 electrosynthesis with the PSE reactor (4 cm^2). The operating conditions were the same as described in Fig. 2.

C15: Fig. 4. Is there a possibility of cations interfering with the PEM?

R15: We appreciate the thoughtfulness of Reviewer 3. Page 19 line 375–380 has been revised to read: “Due to the strong electrostatic attraction between divalent cations/anions and SA/QA groups, divalent cations (e.g., Ca^{2+} and Mg^{2+}) may be stably adsorbed on SA sites of PSE microspheres and PEM, while anions (e.g., SO_4^{2-}) may be strongly adsorbed on QA sites of the AEM. This may interrupt the hopping diffusion of H^+ through the PSE microsphere layer and PEM, as well as the hopping of HO_2^- through the AEM, thus causing the failure of the PSE reactor for H_2O_2 production.”

C16: Line 422. Fig. 6f should be Fig. 6e.

R16: Thank you for the reminder. The typo has been corrected in the revised manuscript.

C17: Please describe in detail the costing process for large area reactors.

R17: Thank you for the suggestion. The costing process for the large area reactors is now described in the SI. SI page 31 line 481–483 now reads: “The EC of H_2O_2 production are calculated using Eq. 6 based on the cell voltages and FEs observed during H_2O_2 electrosynthesis with the PSE reactors of different sizes. The energy cost of H_2O_2 electrosynthesis is then calculated based on the electricity cost of 0.066 USD/kWh.³⁰”

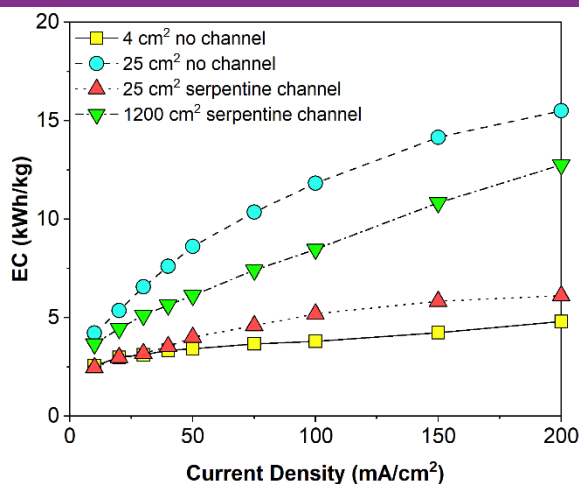


Fig. S29. Energy consumption of H_2O_2 production as a function of applied current densities during H_2O_2 electrosynthesis with the PSE reactors of different sizes.

C18: Please evaluate the stability of the 1200 cm^2 PSE reactor.

R18: Thank you for the suggestion. The stability of the scaled up reactor has been evaluated for the revision as suggested. Page 27 line 500–507 now reads: “To evaluate the long-term stability of the scaled up reactor, it was continuously operated for 480 h under current densities of 25 and 50 mA/cm^2 . Fig. 6f shows that H_2O_2 production were generally stable during the first 408 h, but then decreased gradually. This trend is similar to what has been observed for the small reactor (Fig. 3h) and can be mainly attributed to the gradual degradation of AEM during H_2O_2 electrosynthesis. Overall, the results presented herein indicate that by carefully optimizing the reactor design and operational parameters, the PSE reactor can be successfully scaled up for large applications. Nevertheless, more durable AEMs need to be developed to improve the lifetime of PSE reactors for long-term operations.”

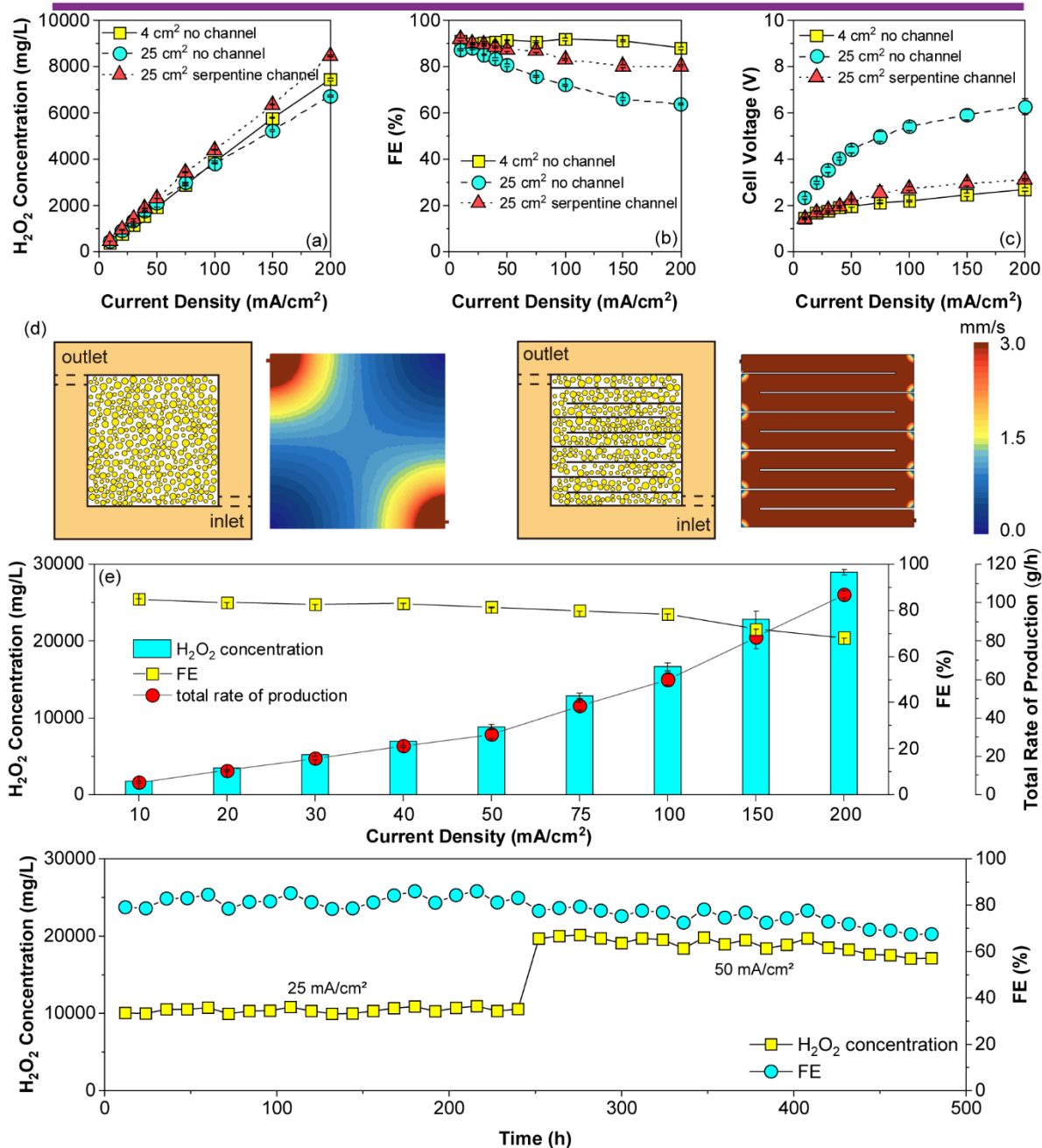


Fig. 6. The influence of reactor scaling-up on H_2O_2 electro-synthesis: (a) H_2O_2 concentrations, (b) FEs, and (c) cell voltages; (d) illustration and computed flow rate of 25 cm^2 reactor without and with a serpentine channel, (e) H_2O_2 concentration, FE, and total rate of production of the 1200 cm^2 PSE reactor with varying current densities, and (f) stability of the 1200 cm^2 PSE reactors during H_2O_2 electro-synthesis with 25 mA/cm^2 (0–240 h) and 50 mA/cm^2 (240–480 h). The DI water flow rate was 1, 5, and 60 mL/min for the 4, 25, and 1200 cm^2 reactors, respectively (Figs. 6a-e), and was 25 mL/min for the stability experiments with the 1200 cm^2 reactor.



We trust that these revisions accommodate the recommendations of Reviewer 3.

Sincerely,

Yujue Wang, Ph.D.

School of Environment

Tsinghua University

Yujue Wang, Ph.D.
Professor
School of Environment
Tsinghua University

December 15, 2024

Manuscript submitted to Nature Communications: **NCOMMS-24-51548A**, entitled “**Optimization and scaling-up of porous solid electrolyte electrochemical reactors for hydrogen peroxide electrosynthesis**”.

Dear Editor,

We appreciate the valuable time that **Reviewer 4** has taken to review this paper. We have accommodated these review comments as follows:

General comments: The manuscript “Optimization and scaling-up of porous solid electrolyte electrochemical reactors for hydrogen peroxide electrosynthesis” provides a systematic study and optimization of a PSE reactor for the electrosynthesis of H_2O_2 . The results show that the PSE with high surface sulfonate group density and the AEM with hydrophilic polymer backbone facilitate the conduction of H^+ and HO_2^- for efficient H_2O_2 electrosynthesis. The use of natural air diffusion cathodes and catalyst-coating membrane anodes allows the PSE reactor to produce H_2O_2 without the need for an air pump to supply oxygen/air or the use of sulphuric acid as a dissolving solution, which greatly simplifies the configuration of the PSE reactor and facilitates its operation. By designing serpentine channels to improve the flow pattern in the PSE layer, the PSE reactor can be successfully scaled up without a significant reduction in the electrosynthesis performance of H_2O_2 . This study is in principle interesting for a wide readership, especially provides an economically competitive and attractive method to produce H_2O_2 . But some of the conclusions are hard to follow and requiring more discussion toward the results. Hence, before considering published in the Nature Communications, following issues need to be addressed:

Response: We appreciate the thoughtful summary and insightful comments of Reviewer 4. We have revised the manuscript to accommodate the comments of Reviewer 1, as detailed below.

Specific comments

C1: In Fig. 3 and Fig. S17, the mean square displacement and radial distribution functions of the two AEMs (Sustainion X-37T and AMI-7001) were analysed. To demonstrate that the experimental tendency of all AEMs can be explained by the mechanism proposed by the authors, please add the data of classical MD simulations for Piperion A-40, Penton 7215-30, FAA-3-50, FAA-3-PK-130.

R1: We appreciate the constructive suggestion of reviewer 4. As suggested, we have added the classical molecular dynamics (MD) simulation results for two AEMs, Piperion A-40 and Penton 7215-30 in Fig. 3 and Fig. S17 of the revised manuscript. However, the molecular structures of the other two AEMs, FAA-3-50 and FAA-3-PK-130, are unavailable due to proprietary reasons. Therefore, we cannot perform the classical MD simulations for the two AEMs.

Meanwhile, to accommodate the other comment (C3) of the reviewer, we have increased the monomer number of simulated systems from 10 to 40 to represent the AEM during the classical MD simulation. Page 31 line 586–594 has been revised to read: “[To assess the \$\text{HO}_2^-\$ conductivity of the different AEMs, MD simulation was performed using the LAMMPS program with a hybrid force field \(TIP4P-2005 for water and GAFF2 for other molecules\). All calculations were performed using isothermal-isobaric ensemble \(NPT\) or canonical ensemble \(NVT\), with a temperature of 298.15 K and a pressure of 0.0001 GPa. The timestep and total simulation time were set to 0.1 fs and 10 ps. The average RDF data was collected from the last 5 ps with every frame. For all calculations, 40 hydroperoxide ions, \$40\lambda\$ water molecules \(\$\lambda\$ is the measured water uptake of AEMs, see SI Table S1 for more detail\), and one polymer of AEM that contains 40 monomers is placed in a box. The \$\text{HO}_2^-\$ conductivity of AEMs is calculated by the Nernst-Einstein equation \(Eq. 7\).⁵³](#)”

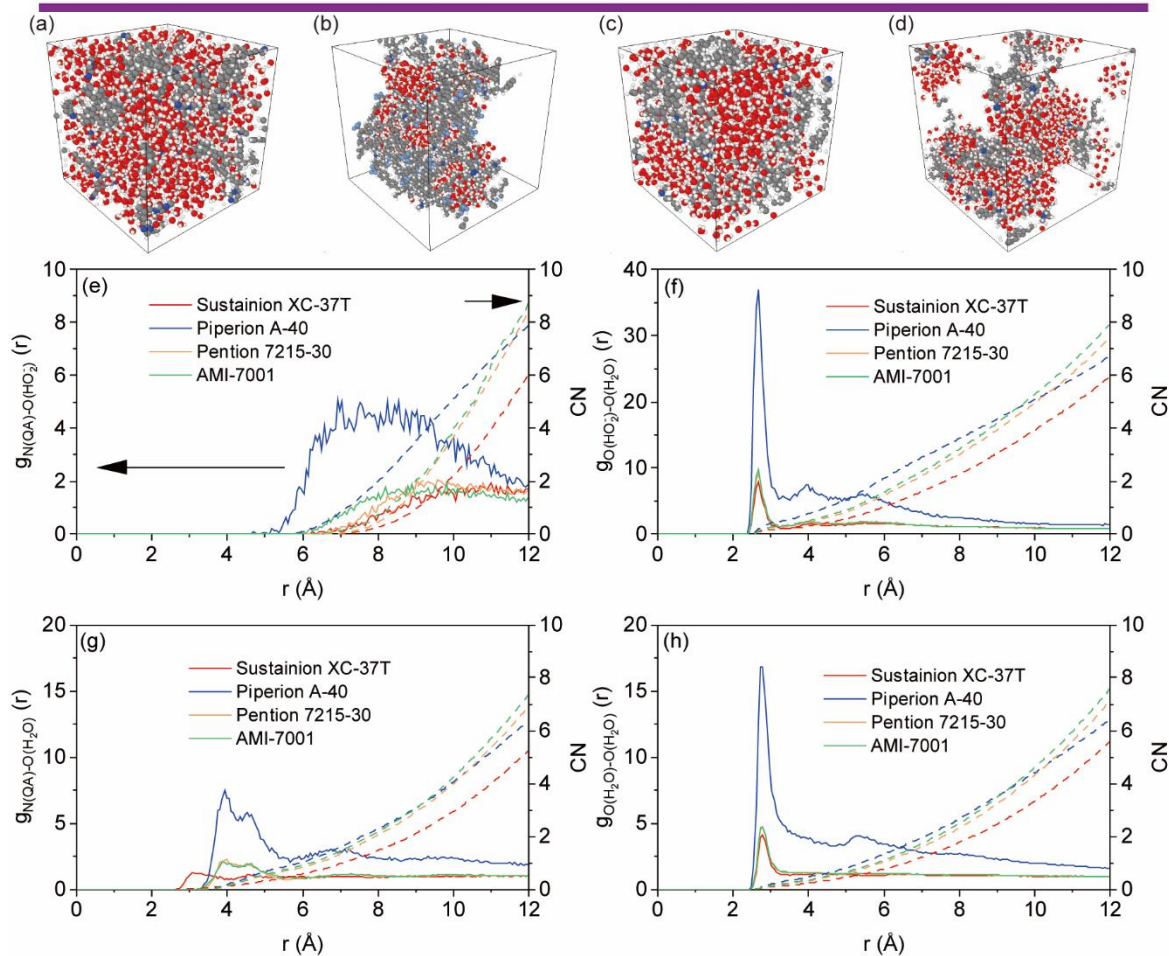


Fig. S17. Pictures of the unit cells used in MD after equilibrium calculations: (a) Sustainion XC-37 T, (b) Piperion A-40, (c) Pention 7215-30, (d) AMI-7001; The RDF and CN of (e) N(QA)-O(HO₂⁻), (f) O(HO₂⁻)-O(H₂O), (g) N(QA)-O(H₂O), (h) O(H₂O)-O(H₂O) of four AEMs.

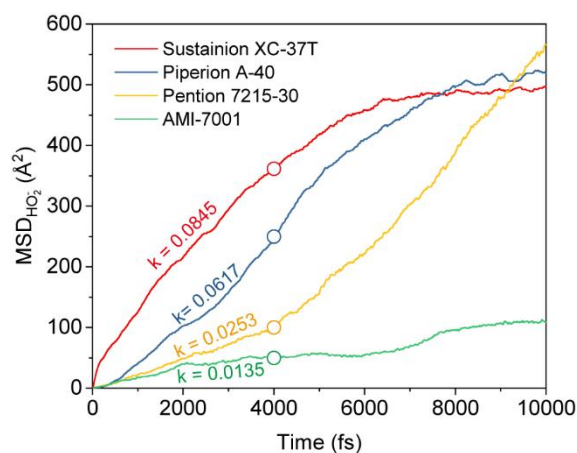


Fig. S18. MSD results and corresponding slopes of various AEMs.



C2: It would be more convincing to find more theoretical support, such as *ab initio* molecular dynamics, for describing how different quaternary amine groups affect the HO_2^- transfer.

R2: Thank you for the suggestion. However, to the best of our knowledge, the Vienna Ab initio Simulation Package usually can only perform an *ab initio* molecular dynamics (AIMD) simulation of a system with a maximum of 200–300 atoms in reasonable timeframe on mainstream dual-socket servers. Furthermore, even with the use of the local-orbital basis, it is difficult to simulate a system with more than 1000 atoms within a reasonable timeframe by AIMD simulation software such as CP2K. On the other hand, a system with even only 10 AEM monomers, 10 HO_2^- , and 10 λ water molecules contains much more atoms, let alone an even larger system the reviewer required (C3). Therefore, it is problematic to simulate the transfer of HO_2^- in AEMs by AIMD simulations. Consequently, HO_2^- transfer in AEMs was simulated in a similar way as many previous studies had done for OH^- transfer in AEMs using the classical MD simulation approach,^{1,2} and we have increased the monomer number of simulated systems from 10 to 40 to more accurately represent the actual material properties of AEMs during the simulation.

C3: In all MD simulations, the authors used the system including only 10 monomers to represent the AEM. In such a small system, it is not possible to accurately simulate its actual material properties. It is better to clarify the reliability of model and method.

R3: We appreciate the thoughtful comments of reviewer 4. The number of monomers has been increased from 10 to 40 for the simulation (see Response to C1).

C4: On page 13, line 251, the authors suggest that the quaternary amine group in AEM affects the strength of hydration of HO_2^- . The stronger the HO_2^- hydration, the greater the electrostatic effect. Please give the relevant theoretical justification on the conclusion.

R4: We appreciate the suggestion of Reviewer 4. In fact, we want to mean the stronger hydration effect, the greater hydrophilic attraction between the QA group and HO_2^- , not electrostatic attraction. We have corrected this typo in the revised manuscript. In addition, to further support this inference, we have calculated the molecular polarity index (MPI) of neighboring atoms around the QA group in the AEM using the Gaussian software and Multiwfn program, and revised the discussion accordingly. Page 12–13 line 238–249 has been revised to read: “Fig. 3 compares several commercial AEMs for H_2O_2 electrosynthesis with the PSE



reactor. As shown, these AEMs exhibited significantly different performances, especially when high current densities (100–200 mA/cm²) were applied to accelerate H₂O₂ production. In general, Sustainion XC-37T achieved the best performance in terms of the concentrations of H₂O₂ product, FEs, cell voltages, and EC, followed in order by Piperion A-40, Pention 7215-30, FAA-3-50, FAA-3-PK-130, and AMI-7001 (Figs. 3a-c and SI Fig. S14). This trend can be mainly attributed to the different conductivity of the AEMs. As shown in Fig. 3d, the R_s of HO₂⁻ conduction of the six AEMs increased in the order of Sustainion XC-37T, Piperion A-40, Pention 7215-30, FAA-3-50, FAA-3-PK-130, and AMI-7001 (see SI Fig. S15 for the Nyquist plots of the AEMs). Therefore, for the same applied current density, the cell voltage during H₂O₂ electrosynthesis will increase in the same order for the six AEMs, as shown in Fig. 3c.

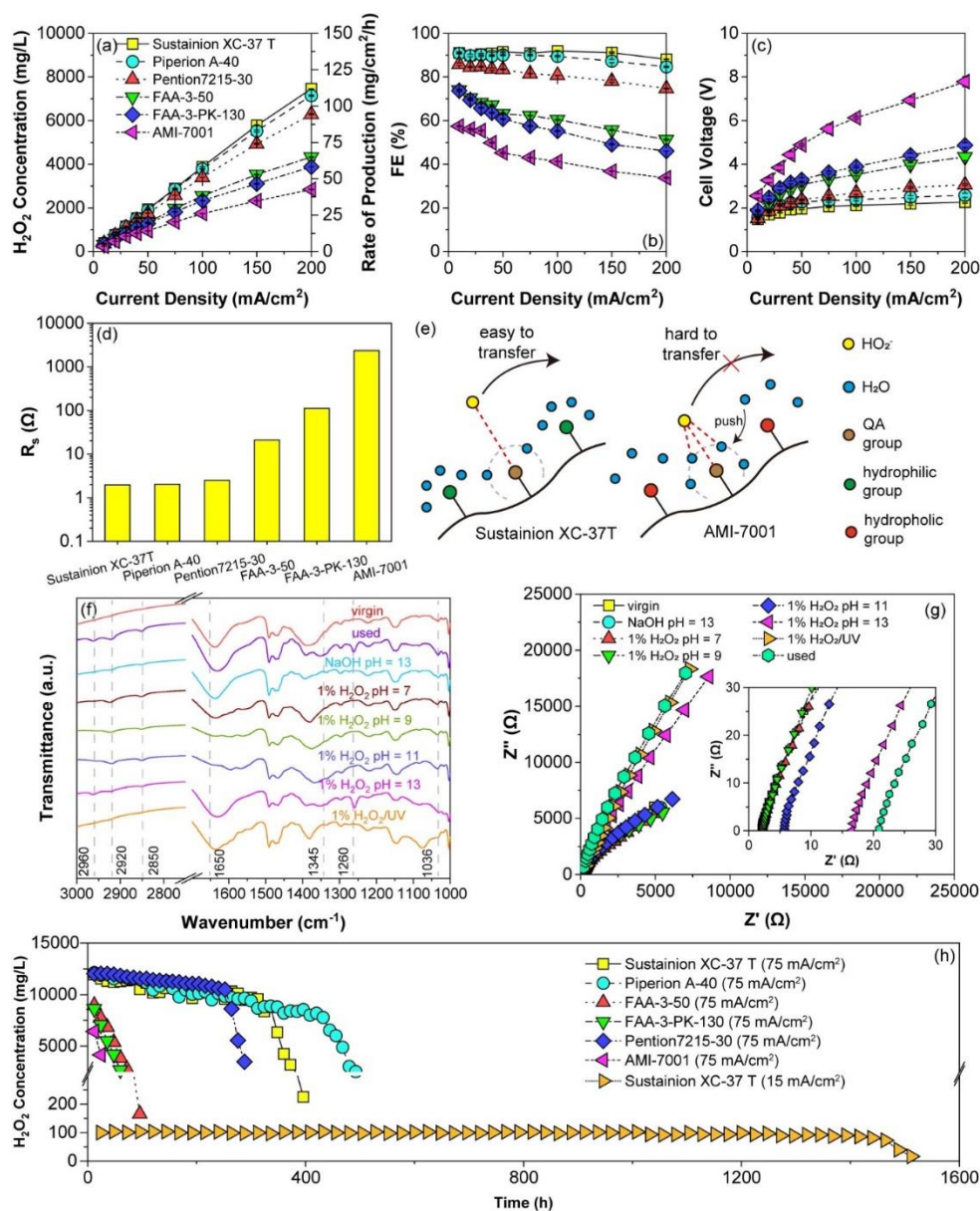


Fig. 3. (a) H_2O_2 concentrations and production rates, (b) FEs, (c) cell voltages as a function of applied current density during H_2O_2 electrosynthesis with the PSE reactor (4 cm^2) with varying AEMs, (d) resistance of HO_2^- conduction of AEMs, (e) illustration of HO_2^- transfer in Sustainion XC-37T and AMI-7001, (f) ATR-IR spectra and (g) Nyquist plots of the virgin Sustainion XC-37T AEM and those used for H_2O_2 electrosynthesis or treated by different processes, (h) stability of PSE reactors during H_2O_2 electrosynthesis with various AEMs at $15\text{--}75\text{ mA/cm}^2$. The operating conditions were the same as described in Fig. 2, with the exception that during the stability experiment at 15 mA/cm^2 , a reverse osmosis filtrate of tap water was used to replace DI water as the feeding water to the PSE reactor.

DFT calculations and MD simulation suggest that the different HO_2^- conductivity of the AEMs can be possibly explained by the differing hydrophilicity of neighboring groups around the quaternary ammonium (QA) in their molecular structure. Although all the AEMs are all functionalized with QA for HO_2^- conduction, their polymer backbones are different (see SI Fig. S16, note that the molecular structure of FAA-3-50 and FAA-3-PK-130 is not openly available yet). For example, the QA group in Sustainion XC-37T is in an imidazole moiety and bridged by a methylene to a benzene ring, whereas the QA in AMI-7001 is directly connected to a benzene ring and three methyl groups. DFT calculations indicate that the neighboring benzene ring of the QA group in AMI-7001 is substantially more hydrophobic than the neighboring groups of QA in Sustainion XC-37T, Piperion A-40, and Pention 7215-30 (see SI Fig. S16 for more detail). As a result, more water molecules will be pushed toward the QA group of AMI-7001, which in turn causes stronger hydrophilic attraction between the QA group and HO_2^- and thus hamper HO_2^- conduction (see Fig. 3e for the illustration). Consistently, the MD simulation show that the coordination number of water molecules around QA of AMI-7001 is higher than that of the other three AEMs (SI Fig. S17g). Meanwhile, the MD simulated HO_2^- conductivity of AMI-7001 (0.85 mS/cm) is considerably lower than that of Sustainion XC-37T, Piperion A-40, and Pention 7215-30 (5.29 , 3.86 , and 1.58 mS/cm , respectively, see SI Fig. S18 for more information). Overall, the simulation results are in line with the EIS measurement (Fig. 3d) and suggest that AEMs with low hydrophobic polymer backbones are beneficial for HO_2^- conduction. This information may provide useful guide for the development of AEMs for HO_2^- conduction.”



C5: The manuscript does not explain some of the mechanisms clearly and contains some spelling errors, which affects the overall quality and readability, such as:

- a) In Fig. 3g, the 1036 cm^{-1} band is proposed to be labelled.
- b) On page 21, line 422, the manuscript refers to figure 6f, but it is absent.
- c) In Fig. S2b, the cathode was only energised with oxygen and no proton source was observed to provide the reaction to produce HO_2^- . The authors should give a clear schematic diagram of local reaction-transport process.

R5: We appreciate the kind reminder of Reviewer 4. As suggested, the 1036 cm^{-1} band has been labelled in Fig. 3f in the revised manuscript. The typo in referring to Fig. 6f has been corrected. In addition, Fig. S1b has been redrawn to more clearly show the main reactions and transfer processes involved in H_2O_2 electrosynthesis with the PSE reactor.

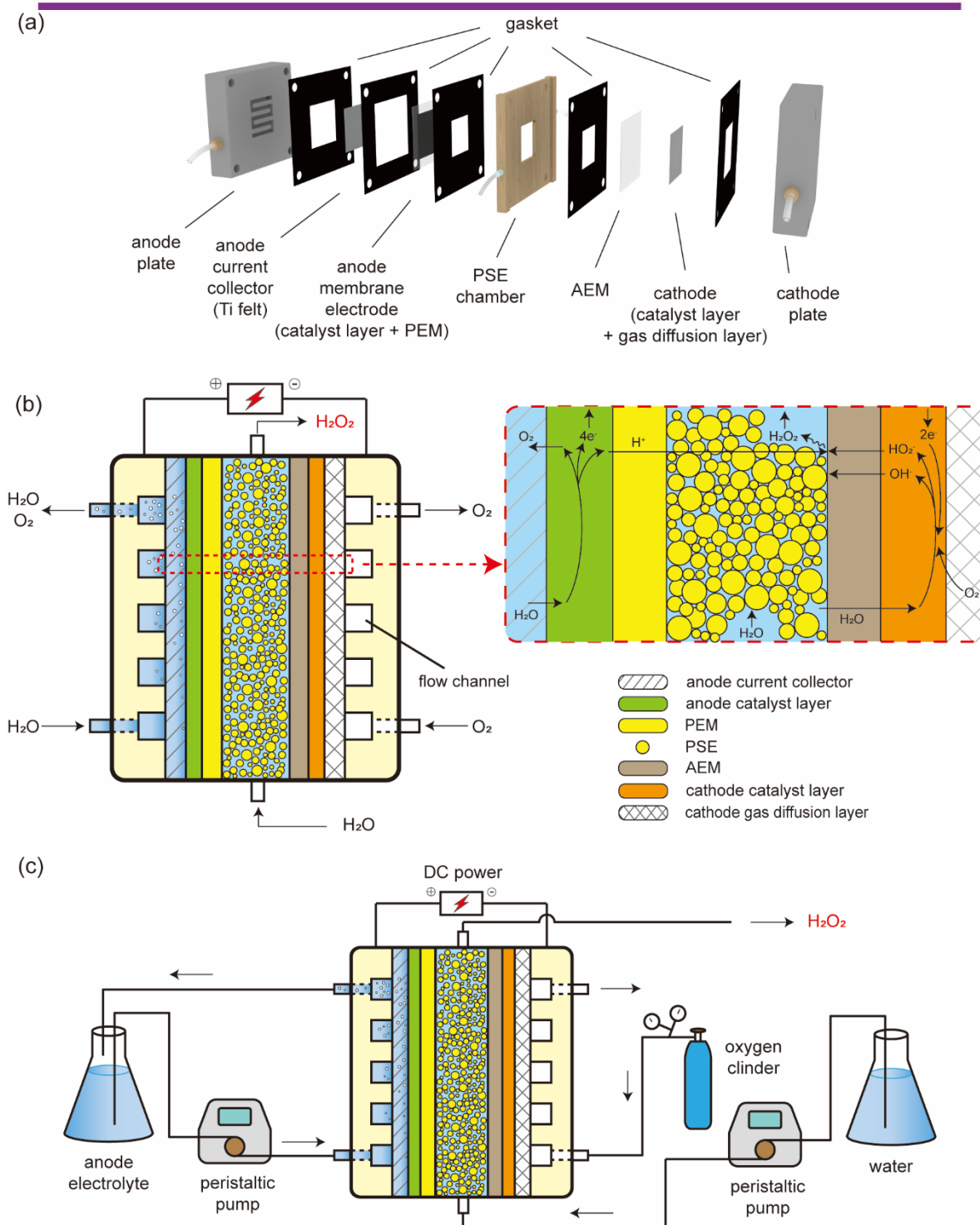


Fig. S1. (a) The components and assembling strategy, (b) H_2O_2 production principle, and (c) operating schematic of the PSE reactor.

We trust that these revisions accommodate the recommendations of Reviewer 4.



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Sincerely,

Yujue Wang, Ph.D.

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References

- 1 Takaba, H., Hisabe, T., Shimizu, T. & Alam, M. K. Molecular modeling of OH⁻ transport in poly(arylene ether sulfone ketone)s containing quaternized ammonio-substituted fluorenyl groups as anion exchange membranes. *J. Membr. Sci.* **522**, 237-244 (2017).
- 2 Rezayani, M., Sharif, F. & Makki, H. Understanding ion diffusion in anion exchange membranes; effects of morphology and mobility of pendant cationic groups. *J. Mater. Chem. A* **10**, 18295-18307 (2022).

Yujue Wang, Ph.D.
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School of Environment
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February 11, 2025

Manuscript submitted to Nature Communications: **NCOMMS-24-51548A**, entitled **“Optimization and scaling-up of porous solid electrolyte electrochemical reactors for hydrogen peroxide electrosynthesis”**.

Dear Reviewer 1,

We appreciate your valuable time in reviewing this paper. We have accommodated these review comments as follows:

General comments: In the revised manuscript, the authors have expanded the electrode area to 100 cm² and designed a 12-unit modular PSE stack with a total electrode area of 1200 cm² for H₂O₂ electrosynthesis, maintaining a stable faradaic efficiency over 500 hours, which is astounding! However, the manuscript does not provide detailed information about the stack’s design or operational parameters, and some data presented is dubious. In my opinion, if the authors have indeed succeeded in constructing this stack and achieving stable operation, it would represent a major breakthrough. That being said, this is precisely why I remain cautious. I believe the authors should provide a video demonstrating the construction and operation of the stack or third-party validation of their results. If the authors can offer this evidence, I would be more than happy to recommend the paper for publication.

Response: We appreciate the comments and suggestion of Reviewer 1. In response to the reviewer’s comments, we have disassembled the PSE stack reactor to show its main components, and then re-assembled it, while using a camera to record the assembly process. It is noted that during the disassembly process, one piece of the PSE chamber was broken when it dropped off the table, and we did not have a new chamber at hand to replace it. Therefore, the re-assembled PSE stack reactor has 10 modular units with a total electrode area of 1000 cm².



The re-assembled PSE stack reactor was then tested for ~100 h operation, which started at 10 pm January 21st and ended at 10 pm January 25th. The stack reactor worked stably at the end of the test, but we had to stop the experiments because it was almost the Chinese New Year (January 29th) and the students had to go back to their hometowns for family reunion. As shown in the attached video, the re-assembled PSE stack reactor operated stably and showed similar performance as the original PSE stack reactor reported in the manuscript.

We believe that these videos clearly show the design, assembly, and operation of the PSE stack reactor, and provide solid evidence that the PSE stack reactor has been successfully constructed for efficient and stable H₂O₂ electrosynthesis.

In addition, we have revised the manuscript to provide more detailed information about the stack's design and operation parameters. Page 25 line 478–481 now reads: “Based on this finding, we further extended the electrode area to 100 cm² and designed a 12-unit modular electrode stack with a total electrode area of 1200 cm² for H₂O₂ electrosynthesis (see SI Fig. S27 and attached video clips for the assembly and operation of the stack reactor).”

SI page 33 line 462–471 has been revised read: “The electrode stack consisted of 12 modular units connected in parallel, and each unit has an effective electrode area of 100 cm². PSE microspheres (Dowex 50W×8, 150–300 μm) were packed with a layer thickness of 2 mm and packing density of ~1100 mg/mL in the serpentine channels between the AEM and PEM (see the video of reactor assembly for more detail). During H₂O₂ electrosynthesis, an oxygen gas (3000 mL/min) and water (25 mL/min) were fed to the cathode and anode of the units, respectively, and DI water (25 or 60 mL/min) was passed through the serpentine channels to collect produced H₂O₂. To prevent overheating of the electrode stack by the Joule heating effect, cooling water (~4 °C) was recirculated through the reactor at a flow rate of ~1000 mL/min using a peristaltic pump (see the video of reactor operation).”

Detailed comments

C1: The authors need to present the flow field design for the large-area reactor. Using a serpentine flow channel raises questions about the uniformity of current distribution and adequate mass transfer across such a large area. According to the supplementary information (SI, Section S6), the oxygen flow rate for the 1200 cm² reactor is specified as 300 mL min⁻¹. Even under ideal conditions of 100% single-pass conversion and 100% FE, this corresponds to an oxygen supply of only 0.0122 mol min⁻¹ (2362.9 C min⁻¹), which supports a current of merely



39.3 A. This translates to a current density of less than 33 mA cm^{-2} , which seems insufficient for the reported performance.

R1: We appreciate the thoughtfulness of Reviewer 1. As suggested, a diagram showing the flow field design has been added in the revised manuscript (see SI Fig. S27c). Regarding the oxygen flow rate of the PSE stack reactor, we are sorry that we made a mistake in the description. The flow rate was actually 3000 mL/min (as shown in the video of reactor operation), not 300 mL/min. The flow rate is able to support a theoretical current of $\sim 400 \text{ A}$, and is sufficient for the applied current tested in this study (12–240 A). We appreciate the carefulness and kind reminder of Reviewer 1, and have corrected the oxygen flow rate to the right value (3000 mL/min) in the revised manuscript (see Response to General comments).

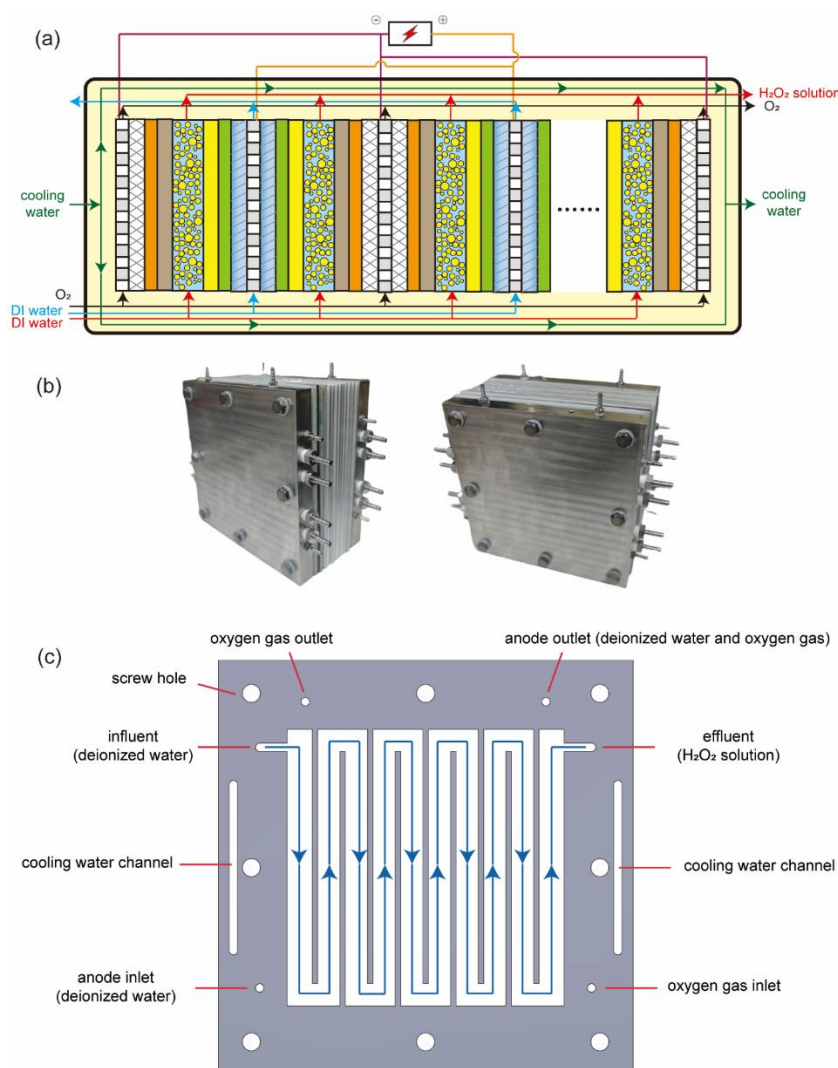


Fig. S27. The (a) schematic and (b) photos of the 12-unit modular electrode stack, (c) the design of flow channel of PSE chamber.



C2: The use of infrared thermal imaging to observe heat effects is of limited value, as it captures the temperature of the reactor's external surface after heat dissipation through the metal casing, which does not reflect the actual conditions at the reaction interface. For instance, in Fig. S28, the maximum observed temperature for the 1200 cm² reactor is only 28.5 °C, which is lower than the maximum temperature recorded in the 4 cm² reactor (Fig. S9d). This discrepancy appears inconsistent. Furthermore, Fig. S28c shows that, with cooling water, the reactor's overall temperature is just 15 °C. The authors should clarify whether such low temperatures affect catalytic performance and consider maintaining a controlled reaction temperature near room temperature to ensure comparability.

R2: We appreciate the thoughtful comments of Reviewer 1. To minimize the electric resistance of PSE layer, the PSE stack (1200 cm²) was designed with a PSE layer thickness of 2 mm. This thickness is insufficient for a thermocouple to be inserted in the PSE chamber to measure the temperature inside the PSE stack. Therefore, the temperature of the PSE stack during H₂O₂ electrosynthesis was measured using infrared thermal imaging.

The thickness of PSE layer of the small PSE reactor (4 cm²) was also set at 2 mm for H₂O₂ electrosynthesis experiments. In addition, in some experiments that were conducted to measure the temperature or pressure inside the reactor, we modified the design of the small reactor and increased the thickness of PSE layer to 5 mm, which allowed the thermocouple or pressure meter to be inserted into the PSE chamber (see SI Figs. S2 and S3). The temperature and pressure inside the small reactor during H₂O₂ electrosynthesis have been reported in the previously submitted manuscript (SI Figs. S9a-c and Fig. S10e).

Nevertheless, re-designing and re-constructing a new PSE stack reactor (1200 cm²) to measure its internal temperature with thermocouples is costly and time consuming. Due to the budget and time limitation, we are unable to do this for the present study.

In general, the PSE reactors worked normally within ~10–25 °C tested in this study, which suggests that the catalytic performance of the reactor will not be considerably influenced in the commonly encountered room temperature range. The effects of more harsh temperature conditions on the performance of PSE reactor for H₂O₂ electrosynthesis will be systematically evaluated in our future studies.

The different temperatures observed for the small reactor (4 cm²) and stack reactor (1200 cm²) are mainly caused by the different room temperatures as the experiments were conducted and the recirculation of cooling water during the experiments of the stack reactor. In response



to the reviewer's comments, we have clarified this issue in the revised manuscript. SI page 35 line 483–489 has been revised to read: “Note that during the experiments conducted with the 4 cm² PSE reactor (June–September, 2023), the room temperatures were $\sim 25 \pm 2$ °C. In comparison, the experiments with the 1200 cm² stack reactor were conducted in November 2023–February 2024, when the room temperatures were about 10 ± 2 °C. In addition, cooling water (4 °C) was recirculated during the experiments with the stack reactor. Therefore, the temperatures measured by the infrared thermal imaging were higher for the small reactor than the stack reactor (Figs. S9d and S28c). In general, the PSE reactors worked normally under the test temperature range of this study.”

C3: The specific methods used to construct the 1200 cm² reactor stack should be disclosed, as many technical details remain unclear. For example, are the individual cells connected in series or parallel? The manuscript states (Page 25, Line 475) that at a current density of 200 mA cm⁻², the cell voltage is 5.5 V. If the cells are connected in series, why is the cell voltage so low? Conversely, if the cells are in parallel, such a high voltage is unexpected. The authors should provide video footage of the stack in operation and present the voltage-time curve for the 480-hour stability test.

R3: Thank you for the questions and suggestion. In response to the reviewer's comments, we have recorded the assembly process of the PSE reactor stack to show the specific methods used to construct the stack.

As shown in SI Fig. S27a, the individual cells of the PSE stack were connected in parallel. We have made it clear in the revised manuscript. SI page 33 line 460–463 has been revised to read: “Based on the optimized reactor configurations determined with the small PSE reactor (4 cm²), a modular electrode stack with a total electrode area of 1200 cm² was manufactured (see Fig. S27a). The electrode stack consisted of 12 modular units connected in parallel, and each unit has an effective electrode area of 100 cm².”

During the 480-hour stability test reported in the manuscript, we recorded the cell voltages in a lab book, but did not use a camera to record the operation process. In response to the reviewer's comments, the cell voltage-time curve of the stability test has been added in Fig. 6f of the revised manuscript. In addition, we have re-assembled the PSE stack reactor and recorded its operation for ~ 100 h using a camera (see Responses to General comments). The cell voltages during the 100-hour test can be seen in the video footage. Under the same applied current



density, the cell voltages of the re-assembled PSE stack reactor are close to the values of the previous stack reactor, confirming the reproducibility of the experiments.

In addition, the reason for the higher cell voltages of the stack reactor (1200 cm²) compared to the small reactor (4 cm²) are discussed in the revised manuscript. Page 25 line 478–481 has been revised to read: “Based on this finding, we further extended the electrode area to 100 cm² and designed a 12-unit modular electrode stack with a total electrode area of 1200 cm² for H₂O₂ electrosynthesis (see SI Fig. S27 and attached video clips for the assembly and operation of the stack reactor).”

Meanwhile, SI page 35–36 line 494–509 has been revised to read: “Cell voltages during H₂O₂ electrosynthesis with the PSE stack reactor are shown in Fig. S29a. For a given applied current densities, the cell voltage of the 1200 cm² stack reactor is higher than that of the 4 cm² reactor and 25 cm² reactor with the serpentine channel, but lower than that of the 25 cm² without the serpentine channel. Increases of cell voltage with increasing electrode sizes in the cell are commonly observed in various electrochemical processes and can be mainly attributed to the increasingly uneven distribution of current on the larger electrode surface.^{30,31} For example, it has been reported that as the electrode area of the PSE reactor was enlarged from 4 to 80 cm², the cell voltage during H₂O₂ electrosynthesis increased significantly from ~2.1 to 5.7 V at the same applied current density of 200 mA/cm².³¹ Many factors can influence the distribution of current and thus the cell voltage during H₂O₂ electrosynthesis, such as the flow patterns, mass transport of oxygen gas, and bubble formation and removal.^{32,33} As shown in Fig. 6d, the introduction of serpentine channel considerably improved the uniformity of flow field in the PSE layer, which helped decrease the cell voltage (Fig. S29a). Additional studies are needed to optimize other factors that can influence the current distribution, and thus further reduce the cell voltage of H₂O₂ electrosynthesis with large electrodes.”

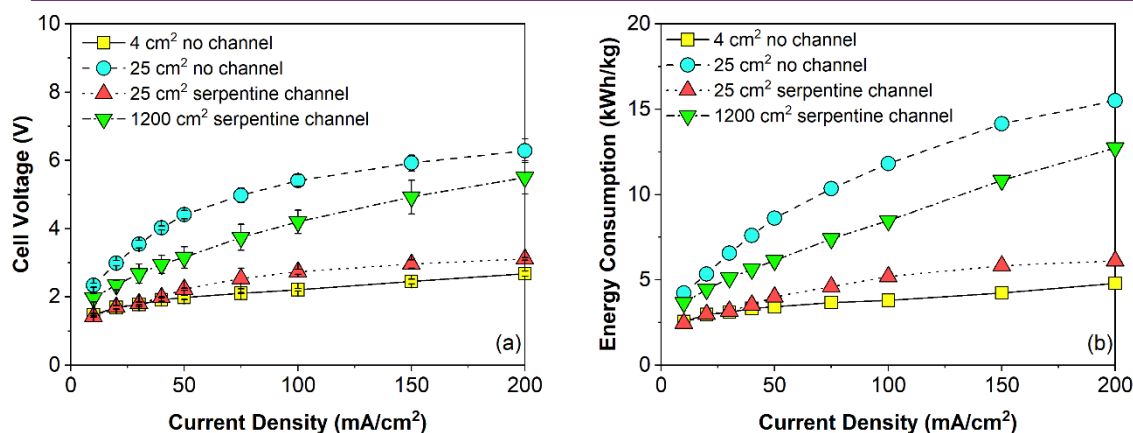


Fig. S29. (a) Cell voltage and (b) EC of H₂O₂ production as a function of applied current densities during H₂O₂ electrosynthesis with the PSE reactors of different sizes.

C4: The flow rate of deionized water in the middle layer of the stack during operation and the pressure distribution in the middle layer are not discussed. These critical experimental details should be provided to ensure reproducibility. While Fig. S29 provides energy consumption data for reactors of different areas, the authors should include the detailed calculation methods used to derive this data.

R4: We appreciate the suggestion of Reviewer 1. The flow rate of deionized water in the PSE layer of stack reactor and other operational parameters have been described in the revised manuscript (see Response to General comments). As explained in Response, to insert a pressure meter in the PSE layer to measure the internal pressure distribution in the PSE stack reactor (1200 cm²), the stack has to be re-designed and re-constructed to increase the thickness of PSE chamber to 5 mm. This is unfeasible for the present study due to time and budget limit. On the other hand, the pressure in the PSE layer of the small reactor (4 cm²) have been measured using a pressure meter and shown in SI Fig. S10e in the previous submission, which can provide some insight on the pressure inside the PSE reactor.

In addition, the detail of energy consumption of H₂O₂ production has been described in the revised manuscript. Page 29 line 569–570 has been revised to read: “The FE, EC, and rate of H₂O₂ production were calculated according to Eqs. 4–6 (see SI S6 for more information).”

SI page 36 line 510–522 now reads: “Based on the applied currents and observed cell voltages during H₂O₂ electrosynthesis, the EC of H₂O₂ production can be calculated using Eq. S21. Meanwhile, the FE of H₂O₂ production can be calculated using Eq. S22.



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$$EC = \frac{10^6 UI}{60cv} = \frac{16666.7UI}{cv} \quad (S21)$$

$$FE (\%) = \frac{nFcv}{MI \times 6 \times 10^7} \times 100\% = \frac{cv}{10575I} \times 100\% \quad (S22)$$

where EC is energy consumption of H₂O₂ production (kWh/kg H₂O₂), U is the cell voltage (V), I is the applied current (A), c is the measured H₂O₂ concentration (mg/L), v is the flow rate (mL/min), n is the electron transfer number for one O₂ molecule reduction to H₂O₂ (n = 2), F is the Faraday constant (96,485 C/mol), and M is the molar mass of H₂O₂ (34.01 g/mol).

By substituting Eq. S22 to S21, the EC of H₂O₂ production can be expressed as Eq. S23 (i.e., Eq. 5 in the manuscript) based on the cell voltage and FE observed during H₂O₂ electrosynthesis.

$$EC = \frac{1.576U}{FE} \quad (S23)''$$

We trust that these revisions accommodate the recommendations of Reviewer 1.

Sincerely,

Yujue Wang

Professor

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Tsinghua University



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February 11, 2025

Manuscript submitted to Nature Communications: **NCOMMS-24-51548A**, entitled
“**Optimization and scaling-up of porous solid electrolyte electrochemical reactors for
hydrogen peroxide electrosynthesis**”.

Dear Reviewer 2,

We appreciate your valuable time in reviewing this paper.

General comments: Authors have addressed the most part of my question, so in my view it
can be accepted.

Response: We appreciate the valuable time that the reviewer took in reviewing this manuscript
and the positive feedback and overall assessment.

Sincerely,

Yujue Wang

Professor

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Tsinghua University

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“**Optimization and scaling-up of porous solid electrolyte electrochemical reactors for
hydrogen peroxide electrosynthesis**”.

Dear Reviewer 3,

We appreciate your valuable time in reviewing this paper.

General comments: All concerns have been addressed and the manuscript can be accepted.

Response: We appreciate the valuable time that the reviewer took in reviewing this manuscript
and the positive feedback and overall assessment.

Sincerely,

Yujue Wang

Professor

School of Environment

Tsinghua University

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Tsinghua University

February 11, 2025

Manuscript submitted to Nature Communications: **NCOMMS-24-51548A**, entitled
“**Optimization and scaling-up of porous solid electrolyte electrochemical reactors for
hydrogen peroxide electrosynthesis**”.

Dear Reviewer 4,

We appreciate your valuable time in reviewing this paper.

General comments: The authors have submitted a revised version of manuscript NCOMMS-24-51548A. The authors responded carefully to all queries and provided additional calculations to support their arguments. The authors have answered all the questions I raised in my initial review of this paper, and I consider the manuscript suitable for publication in Nature Communications

Response: We appreciate the valuable time that the reviewer took in reviewing this manuscript and the positive feedback and overall assessment.

Sincerely,

Yujue Wang

Professor

School of Environment

Tsinghua University